We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

122,000

International authors and editors

135M

Downloads

154
Countries delivered to

Our authors are among the

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Piezoelectric Melt-Spun Textile Fibers: Technological Overview

Dimitroula Matsouka and Savvas Vassiliadis

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.78389

Abstract

Piezoelectricity was first described by the Curie brothers in the late 1800s. The first materials investigated were natural materials such as bone and wood and single crystals such as quartz. Then in 1946 it was discovered that BaTiO₃ ceramic can be made piezoelectric through a poling process. This was followed by the discovery of lead zirconate titanate solid solutions (PZT) in 1954 of very strong lead effects which is still widely used in piezoelectric applications. In 1969, Kawai discovered large piezoelectricity in elongated and poled films of polyvinylidene fluoride (PVDF) opening the way for research into piezoelectric polymers. Piezoelectric polymers exhibit low density and excellent sensitivity and are mechanically tough and respond better to fatigue situations. Since 2010, research has focused on the production of melt-spun piezoelectric textile fibers, with the aim of integrating sensing/energy-harvesting capabilities into smart textile structures. In this chapter, a technological overview of the state-of-the-art research into piezoelectric, melt-spun, textile fibers will be presented. The methods used for the characterization of the fibers will also be discussed with special concentration on the electric response of the fibers after mechanical stimulation.

Keywords: piezoelectricity, textiles, melt spinning

1. Introduction

Piezoelectricity, discovered in 1880 by Pierre and Jacques Curie in quartz [1], is observed in all materials with a crystalline anisotropy. Piezoelectricity has two distinct effects. The direct effect is the polarization of the material under mechanical stress and the inverse effect corresponds to a mechanical displacement when electric polarization is applied to the material [2].



Piezoelectric materials belong to the general group of dielectric materials, electrical insulators that can be polarized by an applied electric field (**Figure 1**). Piezoelectric materials are noncentrosymmetric dielectrics; this means that when subjected to an external electric field, there will be asymmetric movement of the neighboring ions, resulting in significant deformation of the structure; this deformation is directly proportional to the applied electric field [3].

Pyroelectricity, the ability of certain materials to generate an electrical potential when they are heated or cooled, occurs in all materials that belong to a polar crystal symmetry class. It should be noted that, not all non-centrosymmetric classes are polar, not all piezoelectric crystals are pyroelectric. However, all pyroelectric crystals are piezoelectric. Ferroelectrics form a subset of the set of pyroelectrics because they are polar materials in which the direction of the polar axis can be changed by the application of an electric field [4]. Investigation into the piezoelectric properties of materials commenced from materials readily available in nature such as carnauba wax [5], wood [6] and bone [7]. In 1946, it was shown that BaTiO₃ ceramic can be made piezoelectric by an electrical poling process. The first commercial piezoelectric devices based on BaTiO₃ ceramics were phonograph pickups and appeared in the market in about 1947 [8]. An advance of great practical importance was the discovery in 1954 of very strong piezoelectric effects in lead zirconate titanate solid solutions (PZT) [9]. PZT piezoceramics replaced BaTiO₃ ceramics in most applications and PZT remains one of the most popular piezoceramic materials.

PZT is a polycrystalline ferroelectric material. In a ferroelectric material, the internal dipoles of the material can be reoriented by the application of an external electric field, leaving a remnant polarization at zero applied electric field [10]. This remnant polarization also changes with the applied stress and this is how piezoelectricity takes place. Since 1954, there has been

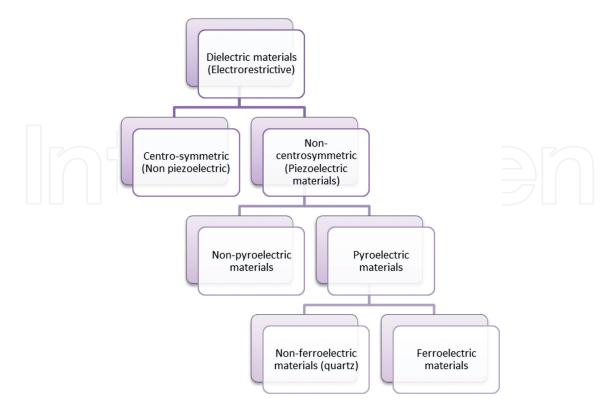


Figure 1. Classification of dielectric materials.

a lot of research to determine the effects of composition (Zr/Ti) and small amounts of additives on the electrical and mechanical properties of PZT piezoceramics [11, 12].

In 1969 Kawai [13] discovered large piezoelectricity in elongated and poled films of polyvinylidene fluoride (PVDF). Research has shown that the polar β -phase of PVDF, which is caused by the application of mechanical stress and/or strong electric fields, is responsible for the development of the piezoelectric property of the material [14, 15].

The piezoelectric behavior of other polar polymers like the odd numbered polyamides such as Polyamide 11 have also been investigated [16–18]. Newman et al. [16] investigated the crystal structure of Polyamide 11, as well as the effect of poling conditions (temperature, time, and poling field), to the overall piezoelectric constants of the material. Polyamide (nylon) is a polymer consisting of the zig-zag chains of CH₂ groups connected by the amide groups (H—N—C=O). The planar sheet structure of molecules is formed by hydrogen bonds between amino groups of adjacent molecules. Scheinbeim et al. [19] used X-ray diffraction to investigate the orientation of the inter-chain hydrogen bonds between the amide bonds, which make up the sheet structure of Polyamide 11, when investigating the polarization of Polyamide 11 in the film form. The planar sheets are oriented parallel to the surface of the film. According to their findings, during poling, the amide dipoles rotate 90° under the strong electric field, which also causes the 90° rotation of the hydrogen-bonded sheets. This rotation results in the 180° rotation of the dipoles.

The molecular structure of odd-numbered (top) and even-numbered (bottom) polyamides is shown in **Figure 2**. In odd-numbered nylons, the electric dipoles formed by amide groups (H—N—C=O) are sequenced in a way that all the dipoles are in the same direction. Therefore, a net dipole moment occurs. In even-numbered nylons, one amide group is in one direction, the next one will be in the opposite direction, alternately. This results in an intrinsic cancelation of the dipole moments [20].

The piezoelectric behavior of polypropylene has mostly been investigated in the case of cellular polypropylene films [21–26], where piezoelectric behavior is a result of the morphology of the structure (air or other gas-filled voids, void morphology, and charge distribution). Other research on the piezoelectric properties of single-film polypropylene or melt-spun polypropylene fibers has been scarce. Research carried out by Kravtsov et al. [27] investigated the polarization of melt-spun polypropylene fibers and concluded that melt-spinning technology favors the formation of spontaneous electret charge in the fibers and that forced fiber polarization in external electric fields gives rise to strong electret effects.

Moreover in the same paper Kravtsov et al. attributed the total electret effect in polypropylene fibers to mechanisms such as Maxwell–Wagner polarization, dipole orientation, and charge carrier injection. Furthermore in 2015, Klimiec et al. [28] investigated the effect of the introduction of SiO₂ and Kaolin fillers on the piezoelectric constant and thermal durability of polypropylene electret, by creating a cellular structure in a single-layer film.

In the research quoted above most of the polymeric piezoelectric materials under investigation were in the film form; however, it is now possible to use polymeric piezoelectric filaments [29, 30] for the applications where flexibility is required, for example, in the interest of producing innovative, "smart" textile products whose components can be integrated into existing textile structures [31–33].

Figure 2. Schematics of molecular structure of odd-numbered and even-numbered polyamides.

While the use of piezoceramic materials such as PZT is extensive, piezoceramics are extremely brittle. Lee et al. [34] compared a PVDF film coated with poly(3,4-ethylenedioxy-thiophene)/poly(4-styrenesulfonate) [PEDOT/PSS] electrodes to films coated with the inorganic electrode materials, indium tin oxide (ITO), and platinum (Pt). When subjected to vibrations of the same magnitude over varying frequencies, it was found that the films with the inorganic-coated electrodes begun to show fatigue cracks at an early stage and at relatively lower frequencies than the PEDOT/PSS film. In further research by Lee et al. [35], piezoceramics tested were susceptible to fatigue crack growth when subjected to high-frequency cyclic loading.

n=1, 2, 3, 4, 5 ...

Moreover, while ceramics have a higher piezoelectric constant, the polymers are more flexible making them more appropriate for areas such as wearable applications [36]. Wearable applications, smart textiles, and e-textiles in general (multifunctional textile products) place specific limitations regarding the rigidity, elasticity, thickness, wearability, comfort, and so on of the

usually fibrous materials to be incorporated in the product, hence the need for piezoelectric material forms that emulate classic textile structures (fibers, yarns, and fabrics). Multifunctional textile materials become increasingly important for combined applications. Piezoelectric fibers and yarns open a new field in the multifunctional textile area, especially for energy-harvesting applications. It is expected that soon a garment using piezoelectric fibers will be developed capable of producing usable electrical power [37].

2. Melt-spun textile fiber materials as piezoelectric elements

In order to obtain usable textile filaments (filaments are a synonym of the word fiber and are specific to continuous fibers vs. staple fibers) from polymers such as PVDF, the polymer must go through a process known as spinning, that is, the transformation (ordering) of the material into yarn. There are several spinning methods applied to polymers that are already in use in the textiles sector. All methods consist of transforming a solution of the polymer, either produced directly from raw materials (direct spinning) or from dissolving/melting the polymer chips (dry spinning, melt spinning and electrospinning).

Both melt spinning and electrospinning can be utilized to produce piezoelectric polymer filaments. The research presented in this chapter is concerned with filaments produced through melt spinning. In melt spinning, polymer chips are melted and then the melt is forced (extruded) through the spinning head called a spinneret. The holes of the spinneret can have different cross-sectional shapes such as round, trilobal, pentagonal, and so on. Each of the cross-sectional shapes has its own advantages regarding the appearance or properties of the filaments produced. Another available fiber structure is the production of bicomponent filaments. Most of the papers analyzed below are concerned with bicomponent filaments. After production, the filaments are drawn and wound unto bobbins. The drawing (elongation) results in the orientation of the macromolecules of the polymer and improves fiber characteristics such as tensile strength. [38, 39].

The process of producing piezoelectric melt-spun textile fibers as described mainly for PVDF includes one more stage after the final drawing stage used during production of the melt-spun fiber. That stage, poling, is a combination of extension, heating, and exposure to high voltage. Extension of the polymer structure (drawing) together with an elevated temperature allows for the transformation from the α -phase crystallites to β -phase. Then, to orient the dipole moments of the β -phase crystallites (rendering the structure as polar), PVDF is subjected to a high electric field. In the specific case of PVDF the stretch ratio and the temperature at which poling is realized affect the maximum β -phase content, which is as previously discussed directly responsible for the development of the piezoelectric property of PVDF [5]. Typical conditions of poling are 80–90°C and the drawing ratio of 5:1 [40–43].

Figure 3 displays the continuous method for the production of melt-spun piezoelectric textile fibers developed at the University of Bolton. Melt extrusion of the fibers is carried out using a single screw laboratory line melt extruder (Plasticisers Engineering, UK). The extruder screw

(diameter of 22 mm) can be operated at speeds up to 50 rpm. The actual speed used for feeding the polymer through the screw is 2 rpm. A flat temperature profile is used for all the polymers consisting of a hopper temperature of 190°C, with a 10°C increment along the barrel and a temperature of 230°C set at the die head.

The apparatus has two water-cooled take-up slow rollers, four temperature-controlled slow rollers, and two fast rollers. The water-cooled rollers are used for the additional cooling of the fiber and temperature-controlled rollers heated the fiber to the required poling temperature, 80°C in this case. The space between temperature-controlled slow rollers and the fast rollers housed a pair of flat-plate electrodes separated by a gap of 10 mm.

To produce the electric field, a Spellman SL300 series high-voltage power supply with a range of 0–20 kV at an output current of 3 mA is used. The poling temperature (80°C) is maintained during the polarization step by heating the bottom electrode. There is a speed difference between the fast rollers and the slow rollers where the speed of the fast rollers is five times higher than the speed of the slower ones, thus obtaining a draw ratio of 5:1. At this point a high voltage of 13 kV is applied. The poling conditions (temperature, extension, and high voltage) are applied simultaneously on the fibers between the temperature-controlled slow rollers and fast rollers [44].

Reviewing the results of the search of the literature, regarding melt-spun textile piezoelectric fibers, it became evident that certain research papers could be considered part of a continuing study into this subject by a specific research team as well as following a specific theme. The research into the development of a piezoelectric melt-spun textile fiber attempts to utilize the accumulated knowledge on the piezoelectricity of thin polymer films and mainly thin films made of PVDF. This explains the concentration of the literature on fibers made of PVDF with very few exceptions, which will be discussed below.

One of the challenges that researchers into piezoelectric textile fibers are faced with is the difficulty of indicating and maintaining the orientation of the fibers with regard to the polarization process. The cross-section shape of the fibers produced is the typical circular cross-section used for the manufacture of synthetic textile fibers. Since the polarization of the fibers is carried out across the thickness of the fiber, the orientation of the charges is along opposite ends of the diameter of the fiber. In a freely twisting and turning fiber, it is quite difficult to

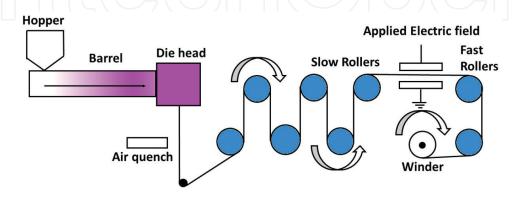


Figure 3. A schematic of the continuous method of production of piezoelectric melt-spun fibers.

determine the position and to orient the theoretical positive (+) side and negative (–) sides of the fiber. Furthermore, the polymer itself, that is, the fiber, has infinite theoretical resistance; this means that the propagation of charges within a complicated structure will be problematic, hence the interest in core-spun fibers with a piezoelectric sheath and a conductive core. A case to point, that will be presented in the following pages, is the work done in France on the production of a piezoelectric coaxial filament, which had a sheath of P(VDF70-TrFE30) (poly(vinylidenefluoride-trifluoroethylene)) and a copper monofilament yarn as core.

As discussed below, the published research is centered mainly on the definition of the parameters for the production of piezoelectric fibers and less on the demonstration of the actual efficacy of the fibers for actual applications (sensors/energy harvesting) or the behavior regarding the aging of the fibers.

Due to the number of researchers working in each team the presentation of the papers that were studied will be geographically grouped (location of the organizations involved in the research).

In Sweden research into melt-spun piezoelectric textile fibers has resulted in a patent [45] and a number of research papers. The first paper, chronologically, by Lund and Hagström [46], investigated the influence of spinning parameters on the β -phase crystallinity of PVDF yarns with no additives or conductive cores. Beginning with the next paper again by Lund and Hagström [47] the researchers introduced the concept of bicomponent PVDF fibers (i.e., PVDF filaments with a conductive core). The conductive cores used in the research originating in Sweden included electrically conductive composites of carbon black (CB) and high-density polyethylene (HDPE) [47, 48], either non-functionalized or amino-functionalized double-wall carbon nanotubes (DWNT) [49] and ethylene-octane copolymer and CB or a high-density polyethylene and again CB [50]. Guo et al. [51] carried out a comparison between three compositions of piezoelectric fibers based on PVDF, that is, PVDF fibers, PVDF/ nanoclay fibers and PVDF/NH2-DWCNT (amino-modified double-wall carbon nanotubes). Finally, in a paper by Nilsson et al. [52] the composition of fibers under investigation is given as a bicomponent with a PVDF sheath and a conductive core while pointing at a previous paper [47] for more information.

Concerning the methods used for the characterization of the fibers (filaments) examined in the papers mentioned above, these are as follows (**Table 1**).

Regarding the research originating in the UK, in 2011, Vatansever et al. [33] published a chapter in the book "Smart Woven Fabrics in Renewable Energy Generation" and the chapter included a presentation of the production method for PVDF piezoelectric monofilament yarns. In 2012, Vatansever et al. [36] presented the production process of a PA-11 (Polyamide 11) piezoelectric monofilament yarn. Vatansever et al. [53] and Hadimani et al. [29] investigated the properties of a PVDF monofilament yarn. In 2015, Bayramol et al. [54] investigated the effect of the addition of multiwalled carbon nanotubes on the piezoelectric properties of polypropylene filaments.

Further on the research carried out in the UK, there was a joint research published that was carried out by researchers based in the UK and researchers based in Greece. The research

Method	Research papers
Differential scanning calorimetry (DSC)	[46-48]
X-ray diffraction (XRD)	[46, 47, 49, 50]
Determination of tensile strength to break	[46, 48, 50]*
Determination of viscosity as a function of shear rate	[50]
Electrical (DC) conductivity measurements	[48, 50]
Determination of the resistance and capacitance of the sensor (individual filament lengths oriented in parallel) and electromechanical characterization of the sensor by subjecting it to a dynamic compression strain perpendicular to the fiber axis	[50]
Determination of the electric signal and strain of a yarn comprising of 24 fibers by subjecting it to a dynamic tensile strain parallel to the fiber/ yarn axis and estimations of the mean power from the fibers	[48]
Evaluation of the sensor (yarn woven into fabric) properties for heartbeat detection	[48]
Characterization of the piezoelectric fibers by connecting the fiber to an impedance analyzer	[52]

Table 1. Characterization methods used in research papers originating in Sweden.

was carried out on piezoelectric melt-spun fibers that were produced based on the process developed by Siores et al. [30] with a composition of PVDF, PP and PA-11 with two different cross-sections (ribbon yarns and cylindrical monofilaments). Matsouka et al. published research concerned with the durability of the electrical response (peak-to-peak voltage) of the fibers after one wash cycle [44] as well as a paper describing a method/device that could be used to measure the electrical power produced by the fibers [55].

The UK-based research/joint research constitutes the only research that investigated materials other than PVDF, namely PA-11 [36, 44, 55] and Polypropylene [44, 54, 55]. They also hold the oldest patent [30] on the production of piezoelectric melt-spun textile filaments, the process described in detail by Hadimani et al. [29]. Vatansever et al. [36] touch on the subject of the amount of energy produced by a single filament versus the energy required for powering small electronic devices, though without providing specific data regarding the energy produced. In contrast, Matsouka et al. [55] provide power measurement results for the three different compositions and two different cross-sections examined.

A significant by-product of the research by Matsouka et al. [44] was a conference paper by Vossou et al. [56] who combined the electrical response (peak-to-peak voltage) produced by the piezoelectric fibers with a computational investigation of the mechanical behavior of the same piezoelectric fibers. Piezoelectric fibers were the subject of modal analysis with the use of the finite elements method to evaluate its eigenfrequencies and mode shapes (modal analysis is the study of the dynamic properties of systems in the frequency domain, a typical example would be testing structures under vibrational excitation).

Furthermore, by comparing the diagram produced by plotting the bending, y-axis, reaction moment developed at the clamped end of the fibers versus time, to the diagram of the deflection of the free end of the fibers, it was found that in the diagram of the bending, y-axis, reaction moment resembled strongly the typical waveform produced during periodic stimulation of piezoelectric ribbon fibers when plotting the voltage versus time. These findings suggested that the production of electric power through the stimulation of the fibers is confined to the clamped area of the fiber, that is, the specific area of the fiber that is being bended (**Table 2**).

In Germany, in 2010, Walter et al. [57] manufactured melt-spun PVDF fibers of textile finesse. Apart from the typical production processes, the produced filaments underwent false twist texturizing. In 2011, Steinmann et al. [58], produced melt-spun PVDF textile fibers using different production parameters. Also in 2011, Walter et al. [59] carried out the characterization of composites made by combining piezoelectric PVDF monofilaments with a two-composite epoxy resin. In 2012, Walter et al. [60] further developed the previous research project [57] by producing both a warp-knitted fabric and two woven fabrics (plain and twill weave). In 2013, Glauß et al. [61] investigated the spin-ability and characteristics of PVDF bicomponent fibers with a CNT/ PP core. This research project is related to research done by Steinmann et al. [62] on the extrusion of CNT-modified polymers. In 2015 Glauß et al. [63] worked on the production and functionalizing of bicomponent fibers consisting of PVDF "sheath" and conductive CNT/PP cores. Also in 2015 Glauß et al. [64] presented their research in the 4th International Conference on Materials and Applications for Sensors and Transducers. The presentation was regarding the poling effect on bicomponent piezoelectric fibers (PVDF sheath with carbon nanotubes as the core).

The research by Steinmann et al. [58] into the phase transitions of melt-spun PVDF fibers was a significant step in determining the effect of process parameters on the crystallinity of

Method	Research papers
Fourier transform infrared spectroscopy (FTIR)	[29, 44, 55]
X-ray powder diffraction (XRD)	[29]
Differential scanning calorimetry (DSC)	[44, 55]
Determination of linear density	[29, 53]
Determination of tensile strength	[53, 54]
Examination of the micro structures of the filaments under scanning electron microscope (SEM)	[29, 53, 54]
Determination of the electric response in Volts of a group of fibers when stimulated by a mechanical stimulus (impact)	[33, 36, 53, 54]
Determination of the electrical response (peak-to-peak voltage) of a single fiber when stimulated by a mechanical stimulus (bending)	[44]
Determination of the electric power (Watts) produced by a single fiber when stimulated by a mechanical stimulus (bending)	[55]

Table 2. Characterization methods used in research papers originating in the UK.

PVDF. The aim of the research was to understand the crystallization and phase transitions in PVDF fibers in order to optimize the formation of the β phase (which is connected to the piezoelectric behavior of PVDF). The research resulted in a detailed overview of the effect of production properties on the phase transformations of PVDF, which is shown in **Figure 4**.

Walter et al. [59] constructed composite specimens using a sandwich of PVDF monofilaments placed parallel to each other and an epoxy resin, placed between copper films. Polarization was carried out on the composite specimens in an oil bath. Determination of the piezoelectric behavior of the samples was carried out both parallel and perpendicular to the fibers. The specimens were subjected to tensile strain and the voltage produced was measured. The results showed anisotropy of the behavior of the composite specimen regarding the voltage produced depending on the direction of the strain (lengthwise or perpendicular to the length) (**Table 3**).

In Portugal, in 2011, Ferreira et al. [65] investigated the effect of processing conditions and a conductive inner core on the electroactive phase content and the mechanical properties of PVDF filaments without a core and with a core containing a conductive PP (polypropylene)/ carbon black composite. In 2013, Silva et al. [66] investigated the effect of repeated processing cycles on crystallinity and the electroactive phase content of recycled PVDF filaments. In 2014, Martins et al. [67] examined the properties of piezoelectric coaxial filaments. The test specimens comprised a piezoelectric cable obtained from a two-layer coextruded filament, comprising an internal semi-conductive electrode (carbon black-filled polypropylene compound and a carbon nanotube-based compound) and a PVDF layer, coated with a thin layer of a

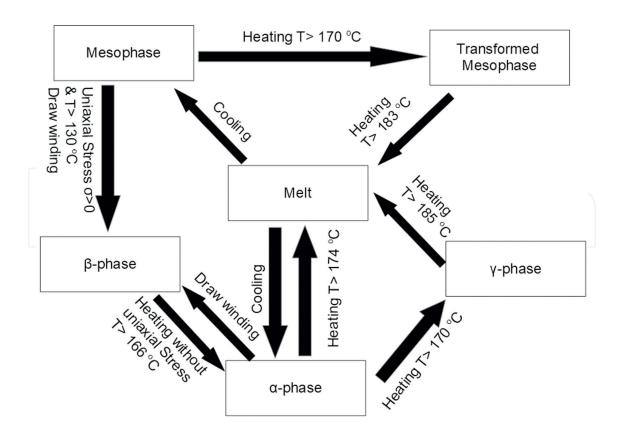


Figure 4. The possible structural phase transitions in fibrous PVDF.

Method	Research papers
Differential scanning calorimetry (DSC)	[57–59, 62]
Wide angle, x-ray diffraction (XRD)	[57–59, 62]
Scanning electron microscope SEM	[57]
Determination of yarn finesse	[57]
Determination of tensile strength at break	[57, 59]
Determination of hot air shrinkage	[57]
Dynamic mechanical analysis (DMA)	[58]
Monitoring of the formation of surface charges on the composites under tensile and bending deformation	[59]
Rheometry measurements	[62]
Transition electron microscopy	[62, 63]
Determination of specific resistivity	[62, 63]
Bright field microscopy	[62]

Table 3. Characterization methods used in research papers originating in Germany.

Method	Research papers
Wide angle, X-ray diffraction (XRD)	[65, 66]
Tensile strength tests to determine the Young modulus of the fibers	[65]
Fourier transform infrared spectroscopy (FTIR)	[66, 67]
Determination of tensile strength at break	[67, 68]
Measurement of the electric conductivity	[67]
Measurement of the electromechanical response (Voltage response of the filaments during mechanical stimulation [tensile strain])	[67]
Microscopy	[67]
Determination of the electromechanical response of the filaments (voltage produced due to mechanical stimulation (vibration, elongation)	[68]

Table 4. Characterization methods used in research papers originating in Portugal.

semi-conductive copper-based lacquer. Also in Portugal, in 2014, Rui et al. [68] investigated coaxial PVDF filaments with a filament core comprising conductive PP. Ferreira et al. [65] concentrated their efforts on producing coaxial piezoelectric filaments made from PVDF, as opposed to pure polymer filaments. The use of a conductive PP/carbon black composite core in the filaments is a common approach in other research, for instance, the work by researchers based in Sweden [48–52] and in Germany [61, 63, 64].

Method	Research papers
Differential scanning calorimetry (DSC)	[70]
Wide angle, x-ray diffraction (XRD)	[70, 71]
Fourier transform infrared spectroscopy (FTIR)	[71]
Determination of tensile strength	[70, 71]
Determination of the sensing capabilities of a woven fabric incorporating the coaxial filaments (voltage response to compression)	[70]
Determination of molecular orientation using optical birefringence	[71]
Determination of the electric response (Voltage) of the piezoelectric fibers integrated in to a woven textile structure after mechanical stimulation (compression)	[71]

Table 5. Characterization methods used in research papers originating in France/joint paper from Australia & Germany.

The subject of the research by Silva et al. [66] (recycled PVDF filaments) was unique in the literature reviewed. The results of several consecutive processing cycles on piezoelectric PVDF samples showed that all the parameters that were studied were unaffected or only very slightly affected by up to nine processing cycles suggesting that PVDF recycling was feasible regarding its electroactive properties (**Table 4**).

In France, Kechiche et al. [69] investigated the properties of a piezoelectric coaxial filament, which had a sheath of P(VDF70-TrFE30) (poly(vinylidenefluoride-trifluoroethylene)) and a copper monofilament as the core. Their work was based on previous research carried out by Khoffi et al. [70] on the production of a polyethylene terephthalate/copper composite filament.

In a joint paper by researchers based in Australia and Germany, Magniez et al. [71] investigated the effect of drawing on the molecular orientation and polymorphism of melt-spun PVDF fibers. The methods used for the characterization of the fibers were (i) the determination of tensile properties of the fibers, (ii) X-ray diffraction (XRD), (iii) Fourier-transform infrared spectroscopy (FTIR), (iv) the determination of molecular orientation using optical birefringence, and (v) the determination of the electric response (voltage) of the piezoelectric fibers integrated in to a woven textile structure after mechanical stimulation (compression).

The approach by Kechiche et al. [69] of manufacturing and studying a coaxial filament (PET/copper) was found to be innovative in the literature reviewed. The research team had to design and develop a new type of spinneret to provide good centering of the inner core (copper filament) in the P(VDF70-TrFE30) matrix copolymer. The research team was able to integrate the monofilament yarns into a woven fabric structure and use the resultant fabric as a pressure sensor (**Table 5**).

3. Conclusions

Based on the analysis of the literature presented in this chapter with regard to the methods of characterization of piezoelectric melt-spun textiles fibers, three main conclusions can be reached: (i) most of the research carried out focuses on PVDF core-spun fibers with very few exceptions. Examples of the exceptions is the research by Bayramol et al. [54] that investigated

the piezoelectric behavior of PP and the work by Matsouka et al. [44, 55] which investigated the behavior of PP and PA-11 fibers as well as PVDF ones, (ii) the majority of the current research utilizes test methods such as XRD, differential scanning calorimetry (DSC) and FTIR to characterize piezoelectric fibers, and (iii) there is no standardized method for the determination of the electrical response of the fibers to mechanical stimulation (neither as a method nor as equipment). Methods such as XRD, DSC, and FTIR aim at the characterization of fiber crystallinity and especially in the case of PVDF, the percentage of β phase, which is the source of the piezoelectric properties for PVDF.

There are two major approaches regarding the characterization of the electromechanical response of the fibers: (i) qualitative tests that are intended to show the potential of the fibers, that is, research conducted by Nilsson et al. and Kechiche et al. [52, 69] and (ii) measurement of the voltage produced by the fibers (or multifilament yarns or fabrics incorporating the said yarns) when they are mechanically stimulated either by tensile strain [48, 67, 68], impact [33, 53, 59], compression [50, 70, 71] or bending [44].

From the electrical point of view, these research approaches restrict themselves in the measurement of the generated voltage, that is, the various piezoelectric fibers were characterized by the maximum voltage generated. Furthermore, in most of the research quoted above, the voltage measurement corresponds to the open-circuit voltage which is used as the main performance indication.

However, considering energy-harvesting applications, the open-circuit voltage is not adequate to characterizing the power-generation capabilities of fibers. For this purpose, knowledge of the current production capabilities of the fibers under load is also required. Research that quotes the measurement of the power produced by the melt-spun piezoelectric textile fibers under load with a description of an innovative method/device developed especially for these fibers can be found in the work of Matsouka et al. [55].

Conflict of interest

There is no conflict of interest.

Author details

Dimitroula Matsouka^{1*} and Savvas Vassiliadis²

- *Address all correspondence to: ptosky@gmail.com
- 1 University of Bolton, Bolton, UK
- 2 Piraeus University of Applied Sciences, Egaleo, Greece

References

[1] Curie J, Curie P. Développement, par pression, de l'électricité polaire dans les cristaux hémièdres à faces inclinées. Comptes Rendus de l'Académie des Sciences. 1880;**91**:294-295

- [2] Jean-Mistral C, Basrour S, Chaillout J-J. Comparison of electroactive polymers for energy scavenging applications. Smart Materials and Structures. 2010;**19**(8):085012
- [3] Abramovich H. Intelligent Materials and Structures. Berlin, Boston: De Gruyter; 2016. p. 378. (De Gruyter Graduate)
- [4] Whatmore RW. Piezoelectric and pyroelectric materials and their applications. Electronic Materials. 1991. pp. 283-290
- [5] Eguchi M. XX. On the permanent electret. Philosophical Magazine Series 6. 1925;**49**(289): 178-192
- [6] Fukada E. Piezoelectricity of wood. Journal of the Physical Society of Japan. 1955;**10**(2): 149-154
- [7] Fukada E, Yasuda I. On the piezoelectric effect of bone. Journal of the Physical Society of Japan. 1957;**12**(10):1158-1162
- [8] Berlincourt D. Piezoelectric ceramics: Characteristics and applications. The Journal of the Acoustical Society of America. 1981;70(6):1586-1595
- [9] Ramadan KS, Sameoto D, Evoy S. A review of piezoelectric polymers as functional materials for electromechanical transducers. Smart Materials and Structures. 2014;**23**(3):033001
- [10] Setter N, Damjanovic D, Eng L, Fox G, Gevorgian S, Hong S, et al. Ferroelectric thin films: Review of materials, properties, and applications. Journal of Applied Physics. 2006;**100**(5):051606
- [11] Heywang W, Thomann H. Tailoring of piezoelectric ceramics. Annual Review of Materials Science. 1984;14(1):27-47
- [12] Jang S-J. Ferroelectrics. In: Kirk-Othmer Encyclopedia of Chemical Technology [Internet]. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2000. DOI: 10.1002/0471238961.0605181810 011407.a01
- [13] Kawai H. A new type of piezoelectricity in elongated polymer films. OYOBUTURI. 1969;38(12):1133-1138
- [14] Davis GT, McKinney JE, Broadhurst MG, Roth SC. Electric-field-induced phase changes in poly(vinylidene fluoride). Journal of Applied Physics. 1978;49(10):4998-5002
- [15] Sencadas V, Gregorio R, Lanceros-Méndez S. α to β phase transformation and Microestructural changes of PVDF films induced by uniaxial stretch. Journal of Macromolecular Science Part B. 2009;48(3):514-525
- [16] Newman BA, Chen P, Pae KD, Scheinbeim JI. Piezoelectricity in nylon 11. Journal of Applied Physics. 1980;**51**(10):5161-5164
- [17] Newman BA, Kim KG, Scheinbeim JI. Effect of water content on the piezoelectric properties of nylon 11 and nylon 7. Journal of Materials Science. 1990;**25**(3):1779-1783
- [18] Takase Y, Lee JW, Scheinbeim JI, Newman BA. High-temperature characteristics of nylon-11 and nylon-7 piezoelectrics. Macromolecules. 1991;24(25):6644-6652

- [19] Scheinbeim JI, Lee JW, Newman BA. Ferroelectric polarization mechanisms in nylon 11. Macromolecules. 1992;25(14):3729-3732
- [20] Su J. Ferroelectric polymers for electromechanical functionality. In: Kim KJ, Tadokoro S, editors. Electroactive Polymers for Robotic Applications: Artificial Muscles and Sensors [Internet]. London: Springer London; 2007. pp. 91-120. DOI: 10.1007/978-1-84628-372-7_4
- [21] Hillenbrand J, Sessler GM. Quasistatic and dynamic piezoelectric coefficients of polymer foams and polymer film systems. IEEE Transactions on Dielectrics and Electrical Insulation. 2004;**11**(1):72-79
- [22] Lekkala J, Poramo R, Nyholm K, Kaikkonen T. EMF force sensor—A flexible and sensitive electret film for physiological applications. Medical & Biological Engineering & Computing. 1996;34(Suppl. 1):67-68
- [23] Neugschwandtner GS, Schwödiauer R, Vieytes M, Bauer-Gogonea S, Bauer S, Hillenbrand J, et al. Large and broadband piezoelectricity in smart polymer-foam space-charge electrets. Applied Physics Letters. 2000;77(23):3827-3829
- [24] Paajanen M, Lekkala J, Kirjavainen K. ElectroMechanical Film (EMFi)—A new multipurpose electret material. Sensors and Actuators A: Physical. 2000;84(1-2):95-102
- [25] Peltonen J, Paajanen M, Lekkala J. Determination of the actuator sensitivity of electromechanical polypropylene films by atomic force microscopy. Journal of Applied Physics. 2000;88(8):4789-4793
- [26] Sessler GM, Hillenbrand J. Electromechanical response of cellular electret films. Applied Physics Letters. 1999;75(21):3405-3407
- [27] Kravtsov AG, Brünig H, Zhandarov SF. Analysis of the polarization state of melt-spun polypropylene fibers. Journal of Materials Processing Technology. 2002;**124**(1-2):160-165
- [28] Klimiec E, Królikowski B, Machnik M, Zaraska W, Dzwonkowski J. Increase of piezoelectric constant and thermal durability of polypropylene electret by introducing SiO₂ and kaolin filler and creating a cellular structure. Journal of Electronic Materials. 2015;44(7):2283-2291
- [29] Hadimani RL, Bayramol DV, Sion N, Shah T, Qian L, Shi S, et al. Continuous production of piezoelectric PVDF fibre for e-textile applications. Smart Materials and Structures. 2013;22(7):075017
- [30] Siores E, Hadimani RL, Vatansever D. Piezoelectric Polymer Element & Production Method & Apparatus Therefor. GB Patent Application 1015399.7. GB 2010
- [31] Siores E, Vassiliadis S, Matsouka D. Energy harvesting and wearable electronics from the textile engineer's perspective. In: eRA-6 International Scientific Conference Proceedings, Athens, Greece; 21-24 September 2011
- [32] Soin N, Shah TH, Anand SC, Geng J, Pornwannachai W, Mandal P, et al. Novel "3-D spacer" all fibre piezoelectric textiles for energy harvesting applications. Energy & Environmental Science. 2014;7(5):1670

- [33] Vatansever D, Siores E, Hadimani RL, Shah T. Smart Woven Fabrics In: Renewable Energy Generation, Advances in Modern Woven Fabrics Technology. In: Vassiliadis SG, editor. IntechOpen; July 27th, 2011. DOI: 10.5772/24790. Available from: https://www.intechopen.com/books/advances-in-modern-woven-fabrics-technology/smart-woven-fabrics-in-renewable-energy-generation
- [34] Lee CS, Joo J, Han S, Koh SK. Multifunctional transducer using poly (vinylidene fluoride) active layerand highly conducting poly (3,4-ethylenedioxythiophene) electrode: Actuator and generator. Applied Physics Letters. 2004;85(10):1841-1843
- [35] Lee JB, Subramanian V. Weave patterned organic transistors on fiber for E-textiles. IEEE Transactions on Electron Devices. 2005;**52**(2):269-275
- [36] Vatansever D, Hadimani RL, Shah T, Siores E. Piezoelectric mono-filament extrusion for green energy applications from textiles. Journal of Textiles and Engineer Tekstil Ve Mühendis. 2012;19(85):1-5
- [37] Jost K, Dion G, Gogotsi Y. Textile energy storage in perspective. Journal of Materials Chemistry A. 2014;**2**(28):10776-10787
- [38] Cook JG. Man-made fibres. In: Handbook of Textile Fibres. 5th ed. Cambridge: Woodhead Publishing; 2005. p. 723
- [39] Mohammadi B, Yousefi AA, Bellah SM. Effect of tensile strain rate and elongation on crystalline structure and piezoelectric properties of PVDF thin films. Polymer Testing. 2007;26(1):42-50
- [40] Gomes J, Serrado Nunes J, Sencadas V, Lanceros-Mendez S. Influence of the β -phase content and degree of crystallinity on the piezo- and ferroelectric properties of poly(vinylidene fluoride). Smart Materials and Structures. 2010;**19**(6):065010
- [41] Murase Y, Nagai A. Melt spinning. In: Advanced Fiber Spinning Technology [Internet]. Cambridge, England: Elsevier; 1994. pp. 25-64. Available from: http://linkinghub.elsevier.com/retrieve/pii/B978185573182050008X
- [42] Sajkiewicz P, Wasiak A, Gocłowski Z. Phase transitions during stretching of poly(vinylidene fluoride). European Polymer Journal. 1999;**35**(3):423-429
- [43] Sobhani H, Razavi-Nouri M, Yousefi AA. Effect of flow history on poly(vinylidine fluoride) crystalline phase transformation. Journal of Applied Polymer Science. 2007;**104**(1): 89-94
- [44] Matsouka D, Vassiliadis S, Vatansever Bayramol D, Soin N, Siores E. Investigation of the durability and stability of piezoelectric textile fibres. Journal of Intelligent Material Systems and Structures. 2017;28(5):663-670
- [45] Hagström B, LUND A, Nilsson E, Ab SI. Method of Producing a Piezoelectric and Pyroelectric Fiber. WO Patent Application WO2014161920A1; 2014. Available from: https://www.google.com/patents/WO2014161920A1?cl=it

- [46] Lund A, Hagström B. Melt spinning of poly(vinylidene fluoride) fibers and the influence of spinning parameters on β-phase crystallinity. Journal of Applied Polymer Science. 2010;**116**(5):2685-2693
- [47] Lund A, Hagström B. Melt spinning of β-phase poly(vinylidene fluoride) yarns with and without a conductive core. Journal of Applied Polymer Science. 2011;**120**(2):1080-1089
- [48] Nilsson E, Lund A, Jonasson C, Johansson C, Hagström B. Poling and characterization of piezoelectric polymer fibers for use in textile sensors. Sensors and Actuators A: Physical. 2013;201:477-486
- [49] Lund A, Gustafsson C, Bertilsson H, Rychwalski RW. Enhancement of β phase crystals formation with the use of nanofillers in PVDF films and fibres. Composites Science and Technology. 2011;71(2):222-229
- [50] Lund A, Jonasson C, Johansson C, Haagensen D, Hagström B. Piezoelectric polymeric bicomponent fibers produced by melt spinning. Journal of Applied Polymer Science. 2012;126(2):490-500
- [51] Guo Z, Nilsson E, Rigdahl M, Hagström B. Melt spinning of PVDF fibers with enhanced β phase structure. Journal of Applied Polymer Science. 2013;**130**(4):2603-2609
- [52] Nilsson E, Mateu L, Spies P, Hagström B. Energy harvesting from piezoelectric textile fibers. Procedia Engineering. 2014;87:1569-1572
- [53] Vatansever D, Hadimani RL, Shah T, Siores E. Characterisation of energy generating polyvinylidene fluoride (PVDF) based piezoelectric filament. Advances in Materials Research. 2011;410:366-369
- [54] Bayramol DV, Soin N, Hadimani RL, Shah TH, Siores E. Effect of addition of multiwalled carbon nanotubes on the piezoelectric properties of polypropylene filaments. Journal of Nanoscience and Nanotechnology. 2015;15(9):7130-7135
- [55] Matsouka D, Vassiliadis S, Prekas K, Bayramol DV, Soin N, Siores E. On the measurement of the electrical power produced by melt spun piezoelectric textile fibres. Journal of Electronic Materials. 2016;45(10):5112-5126
- [56] Vossou CG, Vassiliadis SG, Matsouka D, Siores E. Computational Modelling of Piezoelectric Fibres. In: International Istanbul. Textile Congress 2013 on Innovative and Functional Textiles Proceedings. Istanbul, Turkey; May 30-June 1, 2013
- [57] Walter S, Steinmann W, Gries T, Seide G, Schedukat N, Roth G. Melt-spun polyvinylidene-fluoride fibers of textile fineness. Chemical Fibers International. 2010;60(1):49-51
- [58] Steinmann W, Walter S, Seide G, Gries T, Roth G, Schubnell M. Structure, properties, and phase transitions of melt-spun poly(vinylidene fluoride) fibers. Journal of Applied Polymer Science. 2011;120(1):21-35
- [59] Walter S, Steinmann W, Schütte J, Seide G, Gries T, Roth G, et al. Characterisation of piezoelectric PVDF monofilaments. Materials and Technologies. 2011;**26**(3):140-145

- [60] Walter S, Steinmann W, Seide G, Gries T, Roth G. Development of innovative fibre materials for technical applications—Fine polyvinylidene fluoride filaments and fabrics. Filtration. 2012;12(1):60-64
- [61] Glauß B, Steinmann W, Walter S, Beckers M, Seide G, Gries T, et al. Spinnability and characteristics of polyvinylidene fluoride (PVDF)-based bicomponent fibers with a carbon nanotube (CNT) modified polypropylene core for piezoelectric applications. Materials. 2013;6(7):2642-2661
- [62] Steinmann W, Vad T, Weise B, Wulfhorst J, Seide G, Gries T, et al. Extrusion of CNT-modified polymers with low viscosity—Influence of crystallization and CNT orientation on the electrical properties. Polymers and Polymer Composites. 2013;21(8):473-482
- [63] Glauß B, Bettermann I, Steinmann W, Walter S, Seide G, Gries T, et al. Production and functionalizing of bicomponent fibers based on PVDF. Chemical Fibers International. 2015;66(Yearbook):70-72
- [64] Glauß B, Jux M, Walter S, Kubicka M, Seide G, Wierach P, et al. Poling effects in melt-spun PVDF bicomponent fibres. Key Engineering Materials. 2015;644:110-114
- [65] Ferreira A, Costa P, Carvalho H, Nobrega JM, Sencadas V, Lanceros-Mendez S. Extrusion of poly(vinylidene fluoride) filaments: Effect of the processing conditions and conductive inner core on the electroactive phase content and mechanical properties. Journal of Polymer Research. 2011;18(6):1653-1658
- [66] Silva MP, Martins RS, Carvalho H, Nobrega JM, Lanceros-Mendez S. Extrusion of poly(vinylidene fluoride) recycled filaments: Effect of the processing cycles on the degree of crystallinity and electroactive phase content. Polymer Testing. 2013;32(6):1041-1044
- [67] Martins RS, Gonçalves R, Azevedo T, Rocha JG, Nóbrega JM, Carvalho H, et al. Piezoelectric coaxial filaments produced by coextrusion of poly(vinylidene fluoride) and electrically conductive inner and outer layers. Journal of Applied Polymer Science. 2014;131(17)
- [68] Rui M, Marco S, Renato G, Gerardo R, Miguel NJ, Helder C, et al. Processing and electrical response of fully polymer piezoelectric filaments for E-textiles applications. Journal of Textile Engineering. 2014;60(2):27-34
- [69] Kechiche MB, Bauer F, Harzallah O, Drean J-Y. Development of piezoelectric coaxial filament sensors P(VDF-TrFE)/copper for textile structure instrumentation. Sensors and Actuators A: Physical. 2013;**204**:122-130
- [70] Khoffi F, Khenoussi N, Harzallah O, Drean JY. Mechanical behavior of polyethylene terephthalate/copper composite filament. Physics Procedia. 2011;21:240-245
- [71] Magniez K, Krajewski A, Neuenhofer M, Helmer R. Effect of drawing on the molecular orientation and polymorphism of melt-spun polyvinylidene fluoride fibers: Toward the development of piezoelectric force sensors. Journal of Applied Polymer Science. 2013;129(5, 5):2699-2706