Development of mono-component and tri-component fibres
100% polymer based piezoelectric PVDF to harvest energy

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Abstract. A first study focused on the realization of a 100\% Polyvinylidene fluoride woven fabric. The multi-filaments produced by melt spinning and studied by FTIR, X-Ray and DSC, were optimized in the \( \beta \)-phase, 97\%, thanks drawing ratio of \( \lambda=5 \), and the processing temperature, 90\°C. When the polar \( \beta \)-phase achieves a certain level in PVDF, the woven material is poling with fields up to about 6kV. DMA tests coupled to a Keithley voltmeter allow the solicitation of PVDF fabrics. A variation of voltage is obtained in compression, with a maximum output voltage of up to 2,3V. The other part of the study explains premises of a tricomponent fibre development, PEHD/PVDF/PA12. Two layers of conductive polymers acting as electrodes are placed on either side of the PVDF layer. The interfacial adhesion between the three different layers is analysed by SEM. The maximum stretch on melt spinning was fixed at 2.5 and the \( \beta \)-phase of the PVDF measured by X-Ray.

Introduction

Recovering energy from our environment has become a major research topic over the years. Textile as one of the main interfaces between man and his environment is no stranger to all of this. Thus the smart textiles were interested in this new theme using in particular the movements of the human body. By keeping in mind the electromechanical conversion, since the discovery of the piezoelectric character of Polyvinylidene fluoride (PVDF) in 1969 by Kawai\cite{1}, this polymer is widely used in order to develop energy harvesting systems.

Besides piezoelectric, pyroelectric and ferroelectric properties, many other properties such as high chemical resistance and good thermal stability define the PVDF. Nevertheless PVDF is often studied because of its piezoelectric response. This latter can be obtained when the PVDF crystallizes under the \( \beta \)-phase. Indeed, this polymer has the particularity of being able to crystallize under 2 main phases. The transformation from one phase to another depends on the conditions of application of the material by solvent, melting and stretching techniques or annealing conditions. The main phase, \( \alpha \), also called Form II, trans-gauche conformation TGTG’ (G= gauche, T=trans and G’= anti-gauche) is a non-polar phase due to the placement of the dipole antiparallel, which gives a global dipole moment zero, without piezoelectric property. It is the most stable phase of PVDF and is formed directly from the cooling of the melt. The \( \beta \)-phase, Form I, recognized for its piezoelectric property is of conformation TTTT, all trans. It is the crystalline phase of PVDF with the highest spontaneous polarization. The dipoles associated with the molecules are individually parallel, which allows a non-zero global dipole moment. The principal means to obtaining the \( \beta \)-phase of PVDF is mechanical stress. When \( \alpha \)-phase PVDF is mechanically stretched with a certain drawing ratio at given temperatures, the non-polar \( \alpha \)-phase converts to the polar \( \beta \)-phase. The mechanism of transformation of the \( \alpha \)-phase in \( \beta \)-phase during stretching has been discussed by several authors. It has been shown that the temperature range for obtaining the \( \beta \)-phase varies between 50 and 145\°C \cite{2} for stretching ratios between 1 and 7. Many authors have studied the optimization of this polar phase \cite{3}, like Salimi \cite{4} who exhibits a PVDF film
optimized at 74% β-phase by a ratio between 4.5 and 5 to 90°C. Mohammadi [5] optimizes a film with 86.5% β-phase with a draw ratio of 6.5 to 87°C.  

As a result of the studies on PVDF films, the researchers has turned to the manufacture of 100% PVDF filaments initially in the α-phase which have been extruded and stretched at temperatures and ratio similar to those of PVDF films. By passing through a spinning die composed of holes, the polymer will be transformed into filaments conducted on drawing rollers. During this process, PVDF is subjected to an axial uni-stretch during and after the crystallization leading to a molecular orientation. During stretching between the rollers, α-phase spherulites are stretched transversely in the stretching direction. The chains of α-phase extend more and more until they turn into β-phase [6]. The final crystal morphology is highly dependent on the spinning parameters used. Ferreira [7] shows filaments with a high β-phase rate (≈80%) obtained with a stretch ratio of 5 and temperature between 80°C and 120°C. The optimum stretching conditions were studied and characterised by different experimental techniques such as Infrared spectroscopy [6], X-Ray diffraction (XRD) [8], Wide-angle and small-angle X-Ray scattering (WAXS and SAXS) [8] and differential scanning calorimetry (DSC).

The development of a piezoelectric film or filament requires an electrical polarization step, which is essential to align dipoles. Indeed, during stretching, the molecule is oriented along the stretching direction and the dipoles are oriented perpendicular to the oriented chains. Two main methods are used to polarize and so to aligned the dipoles by subjecting the PVDF to a high electric field : poling by contact or corona [9]. The efficiency of PVDF piezoelectric effect depends on the applied polarization voltage, time and temperature. Mohammadi [5] proposes polarization of its material by discontinuous corona method to an electric field of 1.8MV/cm at 103°C for 10 minutes. A polarization at a temperature between 60°C and 100°C makes it possible to avoid breakdowns [9].

Some authors have developed textile structures with PVDF filaments and measure the piezoelectricity of textile structure to various processes. Soin [10] propose a 3D mesh fabric structure composed of monofilament of PVDF and PA66 wire coated with silver acting as electrodes within the textile structure. By compression, the peak values of the circuit voltage was to14V, at an applied pressure of 0.106 MPa. Krajewki et Magniez [11] propose a PVDF filament woven with conductive fibres for electrodes. The responsiveness of the flexible textile PVDF sensors was tested under impact. The output voltage measured with these sensors was found to reach up to 6 V maximum.

In this study, we aim to develop a fibre based textile structure optimized 100% PVDF piezoelectric and thus measure the output voltage resulting from the mechanical movements of the textile using Dynamic Mechanical Analysis, DMA. FTIR and DSC tests made it possible to evaluate the crystalline structure of polymer.

**Materials and experimental method**

**Materials**

PVDF Kynar 705 was provided by Arkema (France). This polymer melts between 170°C and 175°C and has a density of 1.76 - 1.78 g/cm³.

**Melt-Spinning of the multi-filaments**

The production of the multi-filaments is obtained by melt-spinning pilot, Spinboy I Busschaert Engineering. The PVDF pellets are introduced into a feed hopper and covered in an extrusion screw. Extrusion process allows to melt the polymers through several temperatures zones, between 195-225°C and to pressurize it before passing through the spinneret. The two spinnerets composed of 40 holes each with a diameter of 1.2mm, give shape to the flow of material. At the spinneret exit, an air quenching is carried out in order to solidify the polymer. The rubbery polymer is conveyed to the alimentation roller (R1) and the drawing roller (R2), heated to 110 and 90°C respectively. The stretching rate applied, denoted λ, is the ratio of the speed of drawing roll to the speed of the
alimentation roll. After stretching, the multi-filaments are wound onto a bobbin. Bicomponent and tricomponent multi-filaments were produced using the melt spinning pilot line of CETI (Centre Européen des Textiles Innovants, Tourcoing, France) built by Hills Incorporation. This process is equipped with three single-screw extruders. A tricomponent core/sheath spinneret is adapted to the spinning pilot in order to obtain the tri-component multi-filaments. Overall throughput was adjusted to 0,6g/tr/min.

**Poling**

Poling of textile structure is done in an oven set to 90°C. A high voltage power supply was connected to the textile’s electrodes. The voltage was set to 6kV, which is sufficient to electrically polarize PVDF at this temperature. The sample is cooled before voltage removal.

**Textile fabric weaving**

The samples are prepared in order to have consistent tension, mechanical properties and thickness. The textile structure is woven on hand machine, ARM B60 equipped with the patronic automaton. The weaving was done with 20 yarn/cm on 24 harnesses with a comb of 20 broches/cm.

**Differential Scanning Calorimetry (DSC)**

Crystalline fractions are carried out using DSC (DSC 3+ Netzsch) operating at 10°C/min heating rate. Degree of crystallinity, Xc, can be calculated from the heat of fusion, ΔHm, of the sample to that of a totally crystalline polymer, assuming the same heat of fusion of 100% crystalline, ΔHm0, was given as 104,7 J/g. Equation is:

\[
X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\%
\]  

(1)

**Fourier Transform Infrared Spectroscopy Measurement (FTIR)**

Infrared are equipped with an attenuated total reflectance (ATR) unit. The ATR mode allows a thick sample to be tested by collecting reflection information on its surface. IR spectra were obtained by a FTIR instrument in the 400-1500 cm\(^{-1}\) wave number range. The fraction of β-phase present in each sample can be calculated using the procedure explained by Salimi[4]. Thus, the relative fraction of β-phase, F(β), is calculated as follows:

\[
F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{1,26A_\alpha + A_\beta}
\]  

(2)

where, \(A_\alpha\) and \(A_\beta\) correspond to absorption bands at 766 cm\(^{-1}\) and 840 cm\(^{-1}\) for α and β phases respectively and \(K_\alpha\) and \(K_\beta\) are the absorption coefficient corresponding wave number for each phase (\(K_\alpha=6,1 \times 10^4\) and \(K_\beta=7,7 \times 10^4\) cm\(^2\)/mole).

**Scanning Electron Microscopy (SEM)**

The interfacial adhesion between the different layers in the bi or tri-component is analysed by Scanning Electron Microscopy (JSM-7800F) operating at 5 kV.

**Electromechanical characterization**

For piezoelectric characterization, the textile is subjected to a dynamic compression strain perpendicular to the structure in a DMTA-equipment (DMA TA Instrument Q800), with a plate-to-plate setup. Woven samples fabrics of few millimetres thick are sandwiched between electrodes and compression trays. The electrodes are connected to a Keithley multi-meter (3706A System Switch) to acquire measurements. The force applied by the DMA is between 1 and 5N for a percentage of deformation of 5– 30%.
Results and discussion - Structure textile 100% PVDF

Characterization of the β-phase by RMN – ATR and DSC

Figure 1 shows the FTIR spectra of the multi-filaments stretched at 90°C with a stretching ratio between 2 and 6 at the characteristic wavenumber of the PVDF, such as the peak at 840 cm⁻¹ representative of the β-phase and the 766 and 795 cm⁻¹ peaks of the α-phase. The transformation of α into β-phase is caused by stretching. Indeed, between the stretching ratio 2 and 5, the α-phase decreases in favor of the β-phase. At a stretching ratio 6, the α-phase remains low, but the β-phase begins to decrease. Using Equation (2), the β-phase fraction of each spectrum is calculated and exposed in the table. The total degree of crystallinity measured by DSC is also an important index in order to know the real β-phase rate in the multi-filament. Thanks to these two parameters, it is possible to conclude that the optimized drawing ratio in term of the β-phase is around 5.

![Figure 1](image1)

**Figure 1. (A) FTIR spectrum of the multi-filaments and (B) table of β fraction and crystallinity rate.**

| Draw ratio λ | 2 | 4 | 5 | 6 |
|--------------|---|---|---|---|
| β Fraction, F(β) % | 56 | 87 | 97 | 98 |
| Crystallinity Rate Xc (%) | 51 | 53 | 57 | 55 |

Textile fabric weaving

For the rest of the study, the multi-filaments with an optimal stretching of λ=5, are woven on a handloom. The pattern of the selected fabric is a diagonal interlock across the thickness to obtain a low porous fabric. The sample has an average thickness of 3 mm.

Polarization of the woven structure

The poling, Figure , will accentuate material piezoelectric character by reorienting the macroscopic dipoles. The contact polarization method is used. The textile structure, with a surface area of 9 cm², is entrapped between two circular copper electrodes connected to a voltage generator. Piezoelectric effect’s efficiency of the PVDF also depends on the applied polarization voltage. The voltage was set to 6kV. The cooling is also carried out under electric field. The poling process introduced a radial alignment of the dipoles/crystallites.

![Figure 2](image2)

**Figure 2. Principle of contact polarization equipment.**

Electromechanical characterization

For piezoelectric characterization, the interlock structure was subjected to a dynamic compression in the structure thickness direction using a DMA machine. Distance between the plates is set to 3 mm. Thickness of interlock and the compression force is 4 N. The samples are exposed to a sinusoidal
strain with amplitude of 5%. The electrodes are connected to a multimeter Keithley, which controlled the measurement. The output voltage measured on the interlock is found to reach up to 2 - 3 V.

**Figure 3.** Output voltage measured on the interlock weave upon a 100 Hz frequency, 4 Newton and 5% Deformation spike-shaped stimulus.

This first study on textile structures was carried out in advance of the development of a 100% polymer piezoelectric tri-component in order to better understand the steps of development a piezoelectric textile.

**Premise of the study of the bicomponent and tricomponent piezoelectric multifilaments**

The other part of the study explains premises of tricomponent fibre development. In order to replace the circular copper planar electrodes in the creation of a piezoelectric textile, the project develops a tricomponent fibre: two layers (core and sheath) of conductive polymer composite (CPC) electrodes and the intermediate layer consist of piezoelectric PVDF. The conductive polymers act as an external and internat electrode, making it possible to carry the PVDF piezoelectric response when it is subjected to mechanical stresses. The polymers constituting the electrodes layers were chosen according to their characteristic temperatures, such as the melting point and the crystallization temperature. Indeed, it is necessary to respect a process temperature in order to obtain a strong interface between each polymer. The polymer with the highest crystallization temperature is in the centre of the tricomponent. The right choice of components can improve electrodes sensitivity thanks to an excellent interfacial adhesion.

The cross sections of the virgin bicomponent filaments HDPE/PVDF and PVDF/PA12 and the virgin tricomponent HDPE/PVDF/PA12 were analysed by Scanning Electron Microscopy (SEM) in order to study the interfaces. Based on first visual observations, the interface between HDPE/PVDF polymers, Figure a, seems weaker than the PVDF/PA12 interface, Figure b. The voids underlined, by arrows in Figure , can be due to the different thermal expansion coefficient leading to contraction variation during the melt-spinning process.

The lack of strong interface between the conductive and the electroactive layers can decrease the sensitivity and affect the homogeneity of behavior along the filament. Although the spaces visible in the SEM images are most probably caused by the cutting in nitrogen used in sample preparation, they show a strong potential for layer delamination between HDPE and PVDF.

**Figure 4.** SEM micrographs of fibre cross section with 50 wt. %PEHD/50 wt. %PVDF, x4000 (a) and 50 wt. %PVDF/50 wt. %PA12, x3500 (b).
A study on the interface between the different layers of polymer will be carried out taking into account the surface energies of each polymer. Then the study will be on the spinning of the polymer layers/“fillers” in order to make the PA12 and the HDPE conductive. This tricomponent fibre will have multifunctional properties: conductive and piezoelectric. The textile made from such fibres could be used for mechanical sensor and energy harvesting application.

Conclusion

In this work, textiles structure containing PVDF fibres with a high piezoelectric β-phase content, 97% were developed by melt-spinning, polarization and weaving. Thanks to the temperature and drawing ratios, the crystal chains of PVDF have been optimally stretched to allow the transformation of α-phase into β-phase. These multi-filaments allowed the weaving of a thick textile structure generating a maximum of 3 volts during compression stress. This preliminary study made it possible to highlight the main steps of realization of a piezoelectric textile. In this innovative approach, a piezoelectric tricomponent fibre composed of PVDF and two layers of conductive polymers is being developed.

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