

# CHALMERS



## Development of a piezoelectric polymer fibre

Diploma work in the Master Programme, Advanced Engineering Materials

**DANIEL HAAGENSEN**

*Department of Materials and Manufacturing Technology*

CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden, 2010

Report No. 43/2011

# Development of a piezoelectric polymer fibre

**DANIEL HAAGENSEN**

© **DANIEL HAAGENSEN** 2011

Diploma work no 43/2011  
Department of Materials and Manufacturing Technology  
Chalmers University of Technology  
SE-412 96 Göteborg  
Sweden

Telephone + 46 (0)31-772 1000

## Abstract

Piezoelectric sensors integrated in to textiles are normally in the form of thin films; this study investigates the possibility to manufacture a piezoelectric polymer fibre for true integration into textile materials. The polymer with the strongest piezoelectric effect known today is poly(vinylidene fluoride) (PVDF). To generate piezoelectric properties in PVDF there are two necessary steps: transformation from alpha to beta crystalline-phase and pooling in a high electric field. These steps are known and used today for thin film applications. The manufacturing of a piezoelectric fibre includes those two steps and adds the problem of integrating electrodes to extract the electric output from the fibre.

In this study one linear low density polyethylene (LLDPE) copolymer and one high density polyethylene (HDPE) copolymer mixed with different amounts of carbon black (CB) particles, ranging from 4 – 12 wt-% CB, are investigated for use as inner electrode in a coaxial piezoelectric fibre. The percolation threshold and percolation curve is calculated and the effect of annealing is presented. It was found that over-annealing lowers the conductivity.

Bi-component fibres with a PVDF sheath and a HD/LLDPE +10 wt-% CB conductive composite as core were successfully manufactured by means of melt spinning. Different melt spinning parameters were used to get the highest solid state draw ratio (SSDR) possible. The bi-component fibres were analysed with X-ray diffraction (XRD) which confirmed beta-phase development at higher SSDRs.

The bi-component fibres piezoelectric output was measured in a Dynamic Mechanical Thermal Analysis (DMTA) machine in the case of a simple force sensor manufactured from the fibres. In this case the yarns were embedded in a conductive flexible polymer based coating and compressed in the thickness direction. At the frequency of 10 Hz the sensor had an output voltage of 23mV/N which decreases with increasing frequency.

The piezoelectric output was also measured in a simple tensile test where the fibres were stretched by an oscillatory load at about 5 Hz. The output voltage was in this case found to be proportional to the applied force amplitude. By applying an oscillatory tensile load in the range of 0.25 - 2.5 kg at 5 Hz an oscillatory peak-to-peak voltage in the range 5 - 60 Volts was measured. The output voltage normalised to the stress in the fibres was in the range 10-18 Volts/cN/Tex. A 3500 dtex yarn generated a peak-to-peak voltage of 60V subjected to a load amplitude of 2kg at 5Hz. In terms of tensile strain the output is in the range 1800-3300 volts per unit of tensile strain.

The innovative fibres described seem to have potential in a number of applications including textile sensors, actuators and energy scavengers.

## Acknowledgements

My supervisor, Dr. Bengt Hagström at Swerea IVF, is kindly acknowledged for his enthusiastic support and guidance thru all the different phases of the work spanning from planning to writing the final report. A special thank goes to Anja Lund at Chalmers/Textile college of Borås for updating me on the state-of-the-art as well as the work done up to now on the development of PVDF based electroactive fibres. I am also grateful to Urban Jelvestam at Chalmers for his kind help and instructions regarding XRD measurements. Further appreciation goes to Dr. Christer Johansson at Imego for their help with the piezoelectric characterization. Thank goes also the staff at Swerea (no one forgotten) for their constant support and help during the thesis work. Finally I would like to thank my examiner, Prof. Rodney Rychwalski at Chalmers, for his kind and valuable support.

## Table of content

Introduction.....	1
Background.....	1
Piezoelectricity .....	1
Conductivity.....	1
Experimental .....	2
Materials.....	2
Apparatus .....	2
Small scale compounding .....	2
Grinding .....	2
Sample preparation for conductivity measurements .....	3
Conductivity measurements .....	3
Large scale compounding.....	3
Bicomponent fibre spinning .....	4
X-ray diffraction (XRD).....	5
Annealing.....	5
Pooling.....	5
Sample preparation for piezoelectric response test .....	5
Piezoelectric response measurement .....	7
Results and discussion.....	9
Conductivity of polymer/carbon black composites .....	9
Bi-component melt spinning .....	11
XRD .....	13
Annealing.....	15
Piezoelectric measurement.....	16
Conclusions.....	21
Suggestions for further work.....	21
References.....	22



## Introduction

### Background

Poly(vinylidene fluoride) (PVDF) is characterized as one of the best piezoelectric polymer materials known today (1). This has made it a prime choice for a range of products where ceramic and other piezoelectric materials can't be used because of material properties, for example the brittleness of ceramics. Today commercial products made of PVDF are in the form of thin films and thick cables (2). The films are used for example as vibration sensors and dynamic switch elements and the cables are used as traffic counters where the cable is placed across a road and gives an electric response every time it is compressed by a vehicle. PVDF have other good properties like resistance to solvents, acids, UV-light etc. which also makes it useful in other non piezoelectric product categories.

There is ongoing research to use PVDF in intelligent textile applications in the form of thin films integrated into textiles. Some examples are sensors that can be placed under a bed sheet to monitor the patients breathing and heartbeat, a sensor in a waistband monitoring heart activity and different energy harvesting devices (3). There are piezoelectric fibres for true integration in to textiles but those are generally ceramic based. A piezoelectric polymer fibre is of interest because it would have advantages like high flexibility, low weight and simplified manufacturing. Such a fibre could be waved or knitted directly in to a textile either as part of a bigger textile or as its own textile.

### Piezoelectricity

Piezoelectricity is essentially pressure electricity. This means that when a piezoelectric material is subjected to a mechanical stress it will generate an electric field, known as the direct piezoelectric effect. The effect is reversible, if an electric field is applied to a piezoelectric material it will deform, known as the reversed piezoelectric effect. Mechanical stress in form of tension or compression will generate an electrical field but in reverse directions, this also applies to the reversed piezoelectric effect where the material will contract or expand depending on the direction of the applied electric field. The most common commercial product in everyday life with a piezoelectric material is lighters where the piezoelectric material generates a spark when the button is pushed down.

PVDF's piezoelectric properties was discovered in 1969 and proved to have a relatively high piezoelectric effect (4). The development of piezoelectric properties in PVDF involves two major stages (5). First the polymer has to be mechanically deformed to introduce a phase change in the material, from alpha to beta-phase. Second the beta phase has to be pooled under a strong electric field to generate piezoelectric properties. The mechanical deformation is commonly done by stretching the material at a specific temperature. It has been found that the optimal deformation temperature is in a range between 70-90 °C for maximum beta phase development in the material (3). Pooling of the material can be done in different ways (high electric field, plasma, Corona) and studies have been made to see which way is most efficient (6) (7) (8).

### Electrical conductivity

Conductivity in a non-conductive polymer can be achieved by dispersing conductive filler in to the polymer matrix, creating a conductive polymer composite. This is a widely used and explored method with a wide range of different filler materials available. A common filler is carbon black (CB) which is an amorphous form of carbon with an aggregate size between 10 – 100 nm (9). When CB is well

dispersed in a polymer matrix it will form pathways for electrons to move through the composite, making it electrically conductive. To be able to form these conductive pathways there is a minimum amount of filler needed. This amount is specific for each polymer/filler system. This minimum amount is known as the percolation threshold. In accordance with classical percolation theory for a random system near the percolation threshold, the conductivity follows a power law (10)

$$\sigma = k(w-w_c)^\beta \quad (1)$$

where  $k$  is a constant related to the conductivity of the filler,  $w$  is the weight fraction of filler,  $w_c$  is the weight fraction at the percolation threshold and  $\beta$  is the critical exponent. The percolation threshold can be determined by fitting Eq.(1) to experimental data.

The polymer crystallinity has an impact on the percolation curve. CB particles cannot be accommodated in a polymer crystal and can thus only be found in the amorphous regions. A polymer with a high degree of crystallinity has smaller amorphous regions where all the CB particles gather, resulting in higher conductivity at a given CB concentration in the system.

## Experimental

### Materials

The polymers used were a homopolymer poly(vinylidene fluoride) (PVDF) and two different polyethylene (PE) copolymers. The PVDF was supplied by Solvay Solexis under the commercial name Solef 1006 (MFI=40 g/10 min at 230°C and 2.16 kg, density=1780 kg/m<sup>3</sup>). The melting point of Solef 1006 is 175°C according to the supplier's data sheet. The two PE copolymers were supplied by Dow under the commercial names ENGAGE 8401 (MFI=30 g/10 min at 190°C and 2.16 g, density=885 kg/m<sup>3</sup>) and ASPUN 6835A (MFI=17 g/10 min at 190°C and 2.16 g, density=950 kg/m<sup>3</sup>). The melting point (DSC method) of ENGAGE 8401 and ASPUN 6835A is 80 and 129°C respectively according to suppliers data sheets.

To induce conductivity in the two PE copolymers Carbon Black (CB) supplied by AkzoNobel were used. Commercial name Ketjenblack EC-600JD with the following properties given by supplier: electrical conductivity: 10-100 S/cm, aggregate size: 30-100 nm, apparent bulk density: 100-120 kg/m<sup>3</sup>.

### Apparatus

#### Small scale compounding

Mixing of PE with different weight percentage of CB was done in a Barbender AEV 651 kneader at 180°C. First PE were added and kneaded for 3 minutes at 50 rpm then CB was added and the compound were kneaded for 7 minutes at 100rpm. This was done with both ENGAGE and ASPUN PE copolymers with 4, 6, 8, 10 and 12 wt-% CB. In total 10 different compounds of around 30 grams was produced for conductivity measurements.

#### Grinding

The compounds were grinded to granules in a Rapid granulator.



### Sample preparation for conductivity measurements

Threads, about 1 mm in diameter were extruded at 180°C using a capillary rheometer (CEAST RHEOSCOPE 1000, Italy) using a die of 1 mm in diameter and length of 20 mm. The extrusion speed was 180 mm/min (exit speed from capillary die).

### Conductivity measurements

A set up according to Figure 1 was used for conductivity measurements.

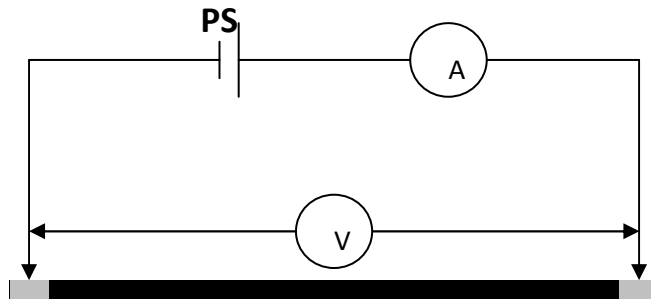


Figure 1. Measurement set up for conductivity measurements.

Extruded threads were contacted by means of crocodile clips at their ends. With this setup voltage and current were measured on three threads of each compound. All measurements were done in a lab with constant air humidity at 30%. The conductivity was calculated as:

$$\sigma_v = I\rho^2 / (Um) \quad (2)$$

Where U is the measured voltage, m the mass of the thread between the clips, I the measured current,  $\rho$  the density of the material and l the length between the clips. The power source (PS in Figure 1) was D400-007D from Oltronix (Em Leek, Holland). The voltage (V in Figure 1) was measured by a Fluke 111 True RMS multimeter from Fluke (Solna, Sweden). The current (A in Figure 1) was measured by another Fluke multimeter.

To measure conductivity on the bi-component yarns the same setup was used but the yarn ends were immersed and coated with silver paint to ensure electrical contact to the core material. In the case of bi-component fibres the conductivity refers to the core material. The amount of core material in the bi-component fibres used for calculating the conductivity was based on the extrusion parameters (volumetric flow rate of sheath and core material at the processing temperature) and density of sheath and core material at the processing temperature.

### Large scale compounding

For bi-component melt spinning more compound than the ~30 grams from the Brabender kneader had to be produced. For this a Coperion ZSK 26 K 10,6 twin screw extruder was used. The barrel temperature profile was set to 155, 195, 205°C starting from the hopper inlet. Screw speed was 200 rpm. The extruded strands were cooled on a conveyor band at room temperature and grinded to granules.

## Bicomponent fibre spinning

The bi-component fibre yarns were produced with a melt spinning line from Extrusion Systems Limited (ESL), Leeds, England.

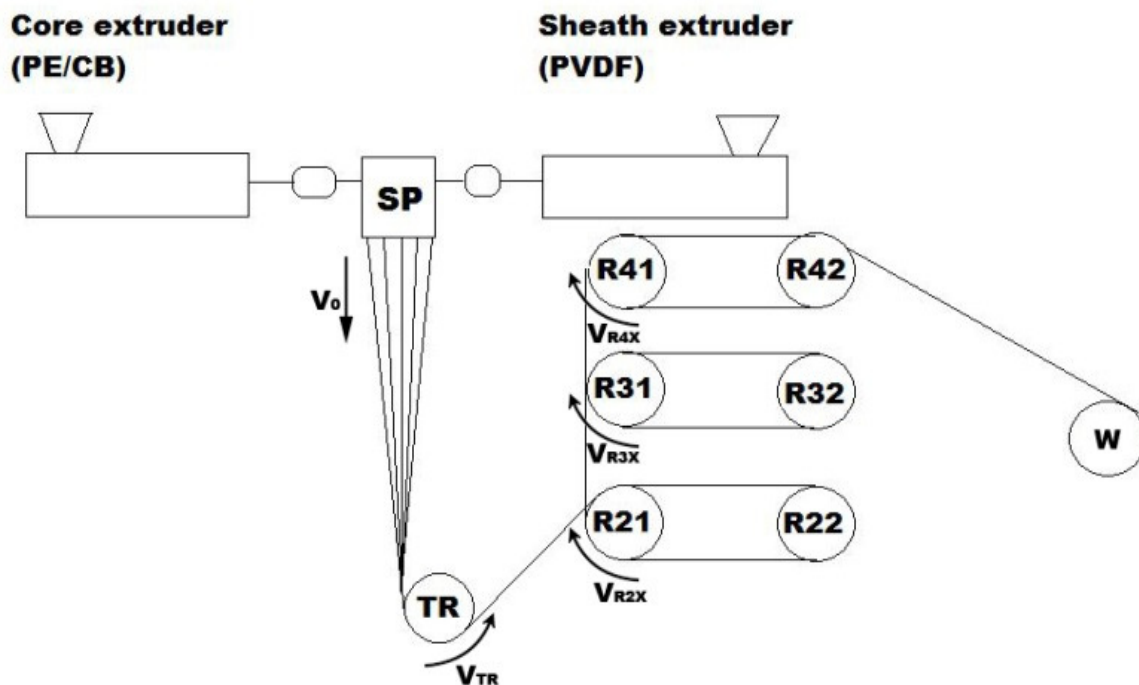


Figure 2. Schematic description of the bi-component fibre spinning system.

The system consists of two single screw extruders, one for core material and one for sheath material. These extruders feed one gear pump each. The gear pumps regulate the amount of material coming in to the spinneret (SP). The spinneret is built so that one material will come out in the centre of a hole and the other material will form around the core material like a skin, producing a bi-component fibre. The main control system controls both the extruder speed and the gear pump speed to ensure that the set value of each material is fed to the spinneret correctly. Between the spinneret (SP) and the Take-off roller (TR) there is a melt drawing zone where the fibres are formed while solidifying. From TR the yarn continues to R21 and R22. R21 and R22 can be varied in roller speed and surface temperature to allow for solid state drawing at a specific temperature. The drawing zone is between R21 and R31, this is achieved by setting a higher speed on R31 then on R21. After drawing the yarn continues to R32 and then back to R31 and then up to R41 and R42 and then finally down to the winder where it is stored on a paper cylinder.

For PVDF/ENGAGE+CB yarns the spinneret used had 48 holes with a diameter of 0.6mm and a land length of 1.2mm each. The temperature settings used were as follows:

Extruder zones 1, 2 and 3: 190°C, 220°C, 230°C, respectively. The set temperature of the gear pumps and spinneret was 230°C.

For PVDF/ASPUN+CB yarns the spinneret used had 24 holes with a diameter of 0.6mm and a land length of 1.2mm each. The temperature settings used were as follows:

Extruder zones 1, 2 and 3: 190°C, 220°C, 230°C, respectively. The set temperature of the gear pumps and spinneret was 230°C.

### **X-ray diffraction (XRD)**

To measure if beta phase was developed in the PVDF during cold drawing a Burker AXS (Madison, Wisconsin) D8 Advanced Theta X-ray diffractometer with monochromator was used. The radiation source was Cr K $\alpha$  with a wavelength of 2.28970 Å. An increment step of 0.1° and a rate of 1 step per 10 seconds were used. The measurements were done in room temperature on a flat sample holder, holding aligned yarns of fibres covering the surface of the sample holder with double-sided adhesive tape. The sample holder rotated at 30 rpm throughout the measurement.

### **Annealing**

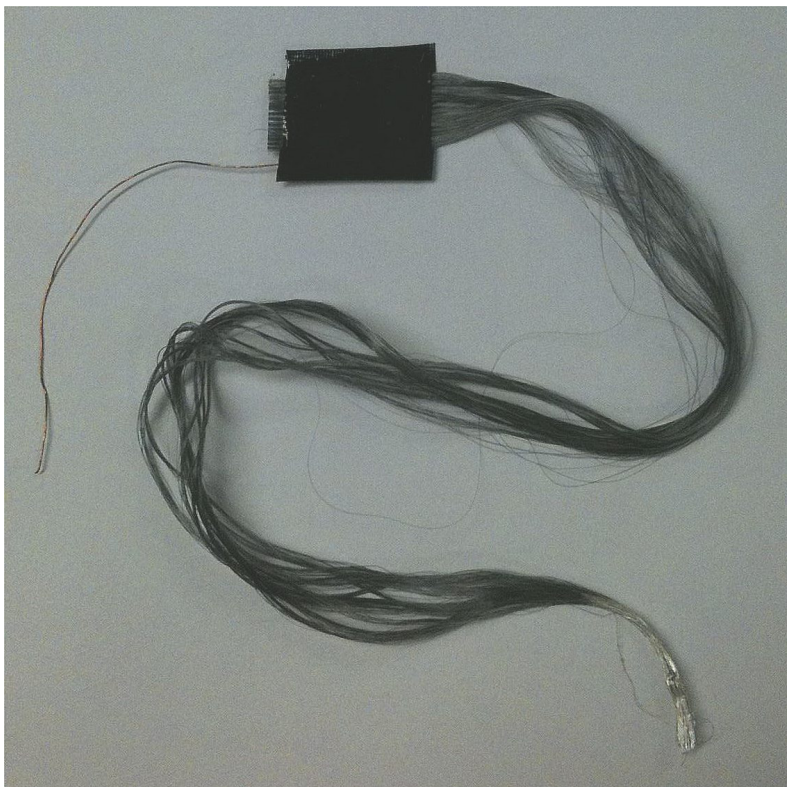
To test if annealing would influence conductivity on the drawn fibres an oven from Heraeus was used. The samples conductivity was measured as described above and then annealed in the oven for 10 minutes at a temperature of  $T_m + 10^\circ\text{C}$  where  $T_m$  is the melting point of the core material. After the samples had cooled off conductivity was measured again.

### **Poling**

For poling a high voltage power supply (ES50P-10W) from Gamma High Voltage Research (Ormond Beach, FL, USA) was used.

### **Sample preparation for piezoelectric response test**

To get an indication of a possible piezoelectric activity of the produced fibres a simple force sensor was manufactured, see Figure 3.



**Figure 3.** Simple force sensor made from bi-component fibres.

A number of flattened yarns were stacked side by side and sandwiched between two thin foils made from Engage 8401 containing 10 wt-% CB. A thin copper wire was also sandwiched between the foils. The sandwich structure was compression molded between two object glasses in a heated press set to 120°C. The foils melt at this temperature and form a conductive matrix surrounding the fibres, see Figure 4.

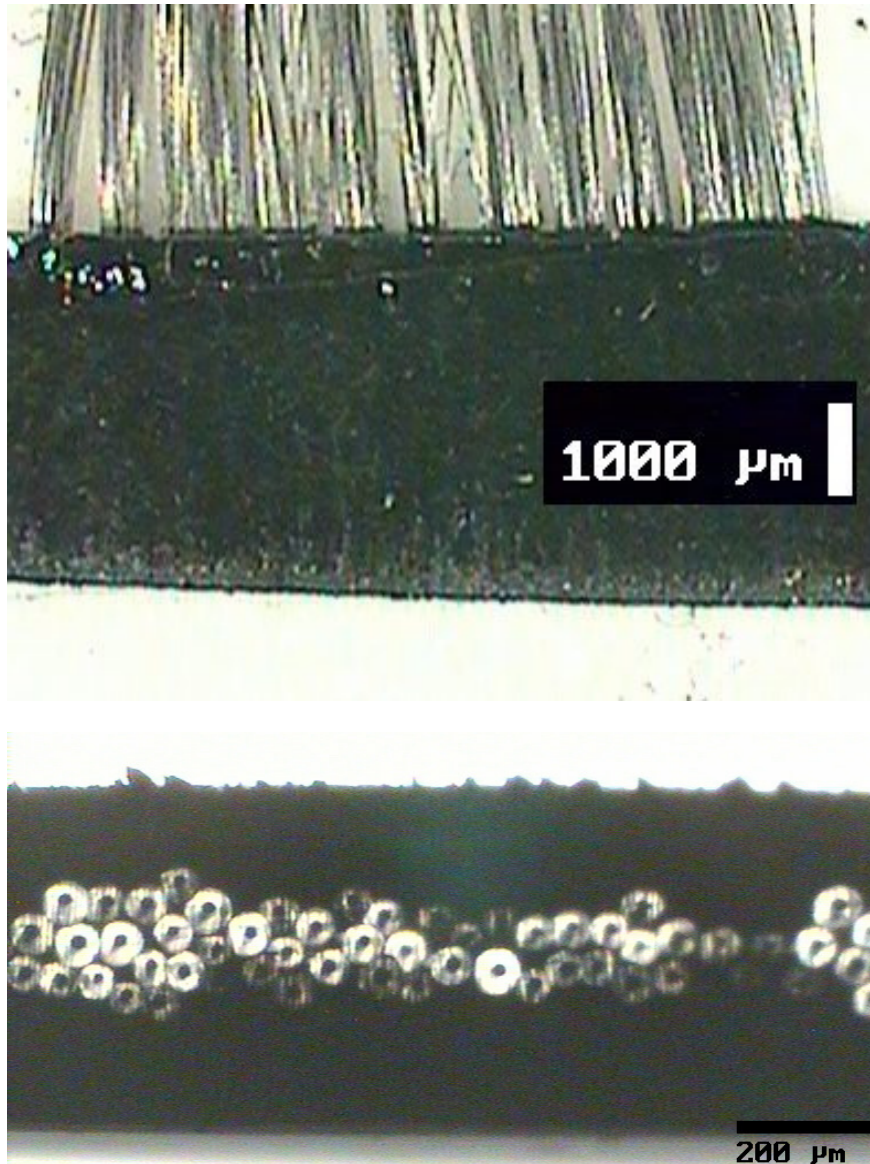


Figure 4. Bi-component fibres embedded in a conductive matrix. Top view and cross section

In this way an outer electrode was formed. The fibre cores were contacted by immersing the yarn endings in conductive silver paint.

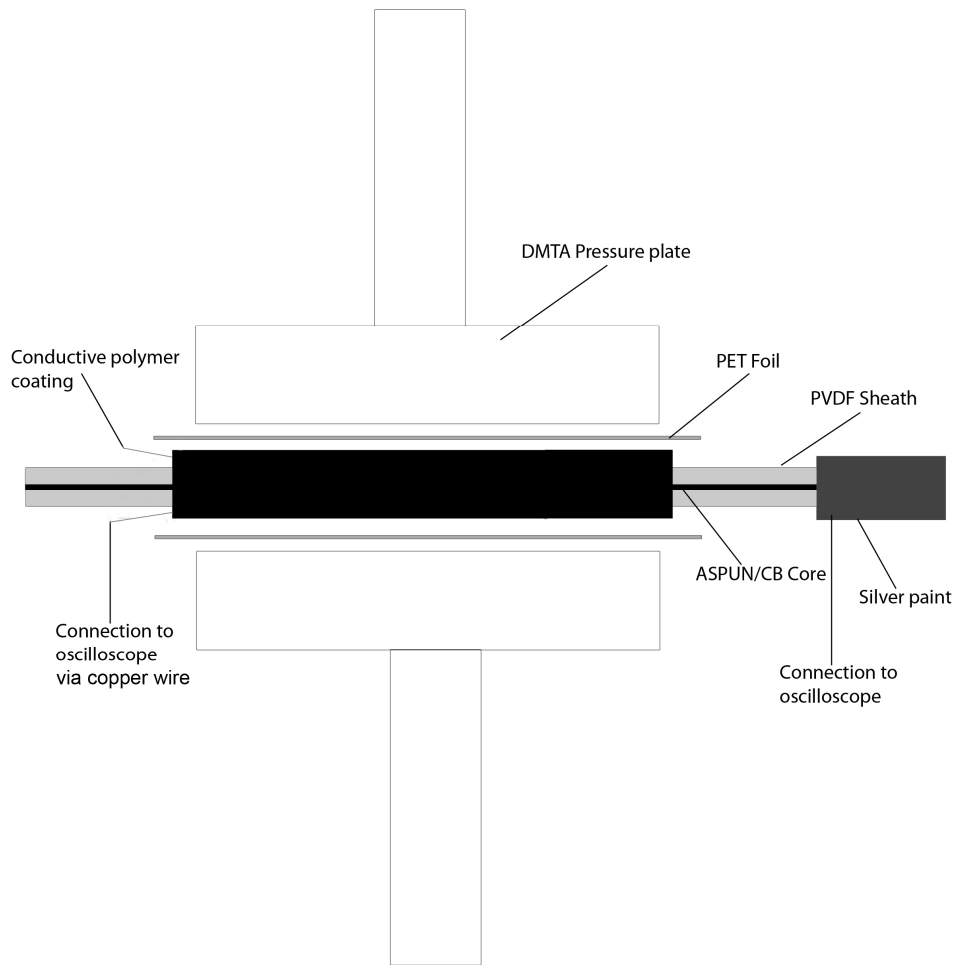
Poling of the sensor was done in an oven at 120°C. The pooling voltage applied over the sensor (clips connected to the silver painted yarn ends and the copper wire embedded in the conductive polymer matrix) was 1000 V. This corresponds to a field strength in the PVDF fibre sheath of about 40-50 MV/m. The voltage was applied until the sample reached room temperature with the oven door opened. Some samples suffered from electrical breakdown which was observed on the built in ammeter which measured current down to 1μA. This is probably because of defects in fibres where

the core material is much closer to the surface resulting in a much higher electrical field at that point (eccentrically placed core). Some samples showed a small signal on the ammeter in the range of 20-100  $\mu\text{A}$  but after a few minutes the ammeter went to zero again. This could be that the point that suffered from break thru might have melted and “repaired” itself.

To evaluate the piezoelectric effect of the fibres in tension along the fibre direction a section of the yarn was simply coated with silver paint forming the outer electrode. The fibre cores were again connected and contacted by immersing one end of the yarn in silver paint after cutting the yarn by a sharp razor blade perpendicular to the fibres direction. The fibres were poled in the same way as the “force sensor” above. However, in some cases it was possible to increase the voltage up to some 1800V without short circuiting the fibres. The field strength was thus almost 80MV/m in this case.

### **Piezoelectric response measurement**

To measure the piezoelectric response of the sensor a Dynamic Mechanical Thermal Analysis (DMTA) machine RSAII (Rheometrics) was used. A DMTA is normally used to record the temperature-dependent visco-elastic properties and determine the storage modulus and the damping value of a material by applying an oscillating force to the sample (11). In this test the DMTA was used to apply an oscillating force at a specific frequency to find the force to output voltage ratio of the sensor. A schematic of the test setup can be seen in Figure 5 below. It should be noted that the DMTA used is only calibrated up to a frequency of 17 Hz and thus the results from tests with higher frequencies in this report should not be referenced.



**Figure 5. Schematic picture of the set up for measuring the piezoelectric response**

The DMTA pressure plates are pushed together compressing the sensor with an oscillating force at a prescribed frequency. The isolating layer (PET-foil) is used to avoid a back current into the DMTA pressure plates that are made of steel. The conductive polymer matrix is used as an outer electrode connected to the oscilloscope with a copper wire. The conductive silver paint is used to connect the inner electrode to the oscilloscope. The force signal from the DMTA was also connected to the oscilloscope facilitating the simultaneous recording of force and output voltage.

In a second test a yarn bundle was subjected to a varying tension in a simple hand test. In this case an outer electrode was applied by means of silver paint, see Figure 6.

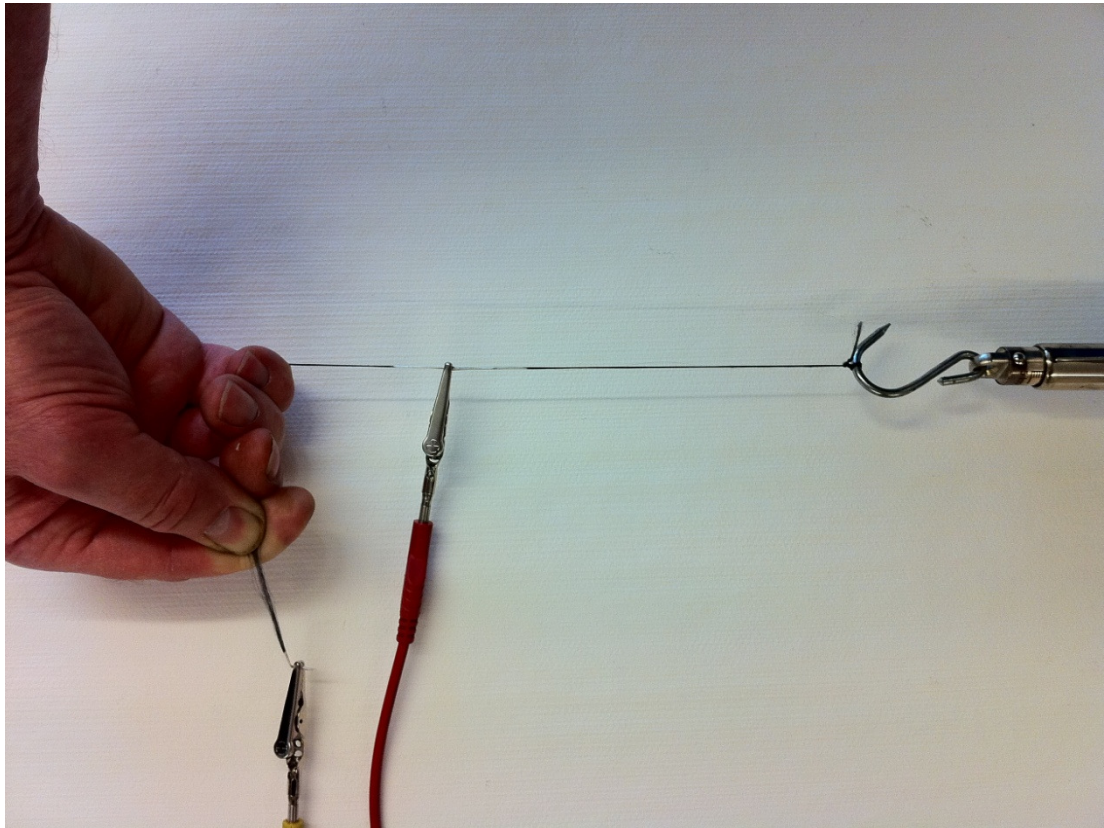


Figure 6. A yarn bundle stretched by hand. The fibre cores were connected by silver paint (inner electrode). A part of the yarn bundle was coated with silver paint as the outer electrode. The two electrodes were connected to an oscilloscope.

The outer and inner electrode was connected to a high impedance ( $1\text{ M}\Omega$ ) oscilloscope. The yarn bundle was stretched by hand in a periodic fashion at a frequency of about 5 Hz. The force applied was estimated by means of a dynamometer and the maximum peak-to-peak voltage was read from the oscilloscope.

## Results and discussion

### Conductivity of polymer/carbon black composites

The conductivity was measured on three different samples from each of the five composites ranging from 4 wt% CB to 12wt% CB. The data presented in Figure 7 are from the small scale mixing with the Brabender kneader. The values indicated are mean values from three different samples of each composite. The constants in Eq.(1) were determined by fitting a line (solid lines in Figure 6) by means of least squares regression, maximizing the square of the correlation coefficient ( $R^2$ ) by adjusting  $w_c$ . By this  $k$ ,  $\beta$  and  $w_c$  (see eq. 1) were determined in a non-arbitrary way.

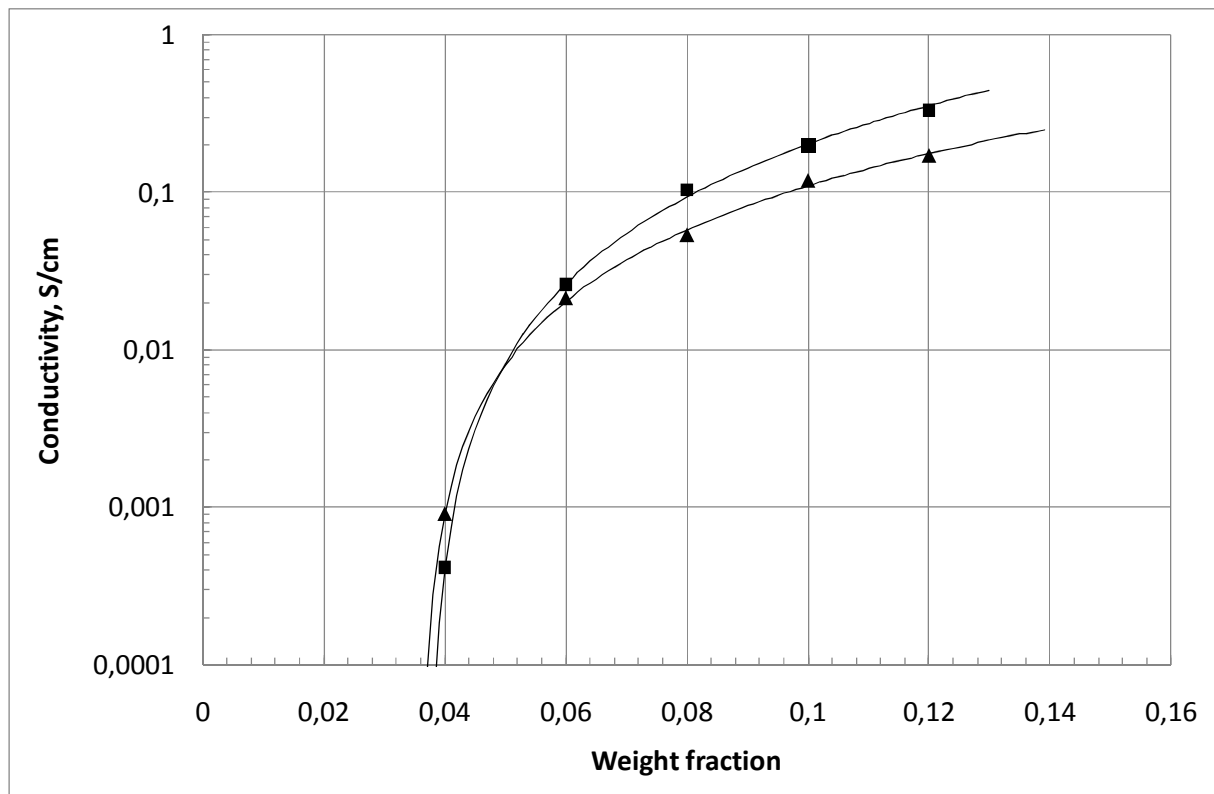


Figure 7. Conductivity vs. weight fraction of CB, Squares indicating ASPUN based composites, Triangles indicating ENGAGE based composites. Lines indicates calculated percolation curve (Eq 1)

The percolation thresholds of the Engage and Aspun composites were in this way determined to be about 3.6-3.7 wt-%. It should be pointed out that the conductivities measured at 4 wt-% CB are rather uncertain also rendering the calculated percolation threshold uncertain. The standard deviation at 4 wt-% CB was about 70% of the mean value for Engage and 25% for Aspun composites while it was about 10 and 3% at 6 wt-% CB respectively. At 10 wt-% CB the corresponding figures were 4 and 3%. The critical exponents for Aspun/CB and Engage/CB were 2.0 and 1.7 respectively.

Both ENGAGE and ASPUN are conductive when mixed with carbon black over the percolation threshold. ASPUN and ENGAGE have similar percolation curves, however ASPUN have higher conductivity then ENGAGE at the same CB wt% content. This can be explained by the higher crystallinity in ASPUN compared to ENGAGE.

Figure 8 and Figure 9 compares the conductivity of large scale mixed composites (twin screw) with small scale mixed composites (Brabender kneader).



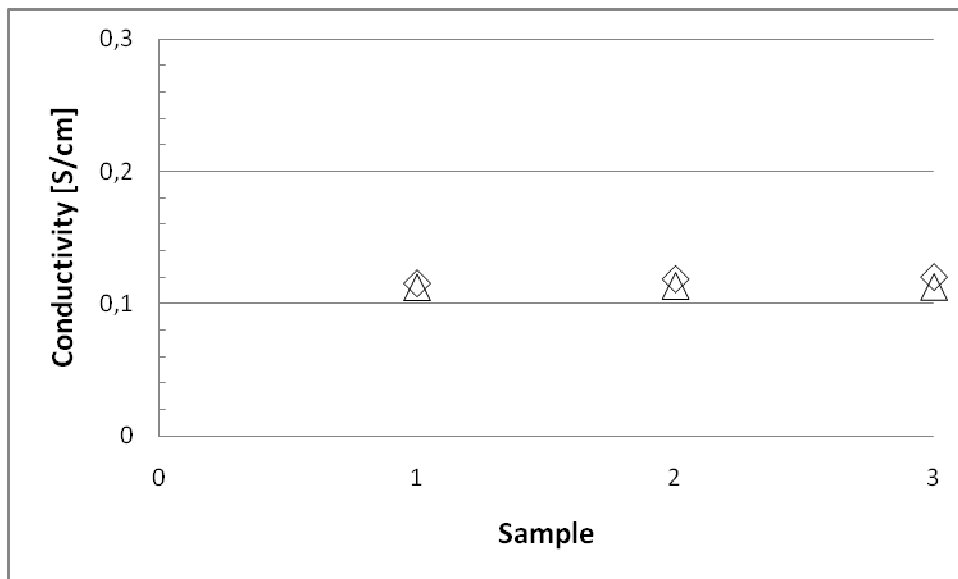


Figure 8. Conductivity of samples from Brabender kneader (◊) and twin screw extruder (Δ). 10 wt-% CB in Engage 8401

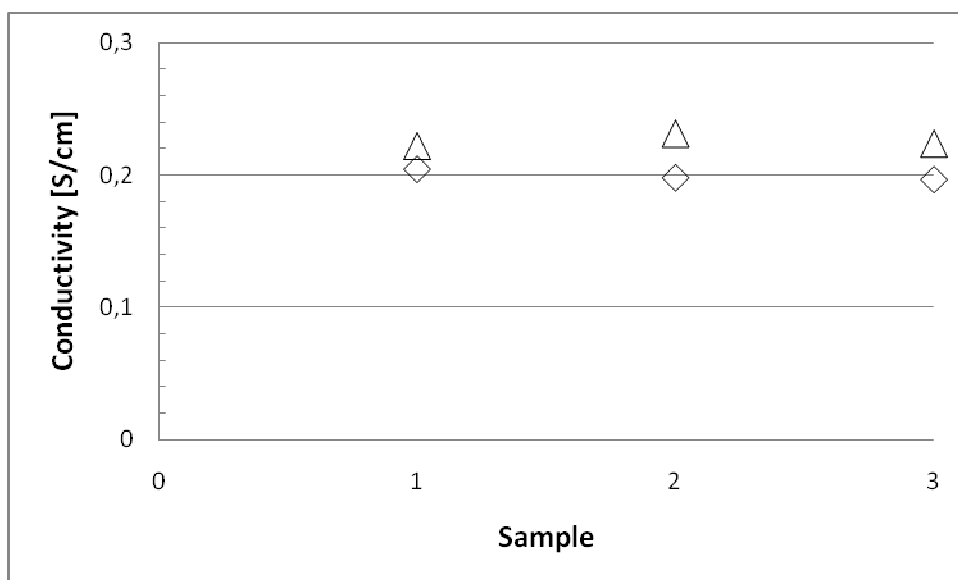


Figure 9. Conductivity of samples from Brabender kneader (◊) and twin screw extruder (Δ). 10 wt-% CB in Aspun 6835A

In case of Engage the conductivity was independent of mixing method while the twin screw compounding produced somewhat higher conductivity for the Aspun composite.

### Bi-component melt spinning

Engage and Aspun with 10 wt-% CB was used to produce bi-component fibres with PVDF forming the sheath. This choice was based on earlier experience at Swerea IVF showing that 10 wt-% CB in PP was spinnable into bi-component fibres with a PA6 sheath (12). Engage based fibres were spun with four different combinations of melt draw ratio (MDR) and solid state draw ratio (SSDR) while keeping the total draw ratio (MDR x SSDR) approximately constant, see Table 1. The highest SSDR shown (4.5) represents the maximum attainable SSDR before frequent spin line breakage occurs. Aspun based

fibres were produced starting at SSDR 4 and then increasing to the limit (4.75) just before spin line breakage occurs.

**Table 1. Fibre production parameters. The volumetric flow rates at the processing temperature were calculated from the gear pump speeds.  $MDR=V_{TR}/V_0$  and  $SSDR=VR_{3X}/VR_{2X}$ . For definition of symbols see Figure 2**

Yarn	MDR	SSDR	Flow rate core ( $\text{cm}^3/\text{min}$ )	Flow rate sheath ( $\text{cm}^3/\text{min}$ )	$V_0$ (m/min)	$V_{TR}$ (m/min)	Temperature R2x (°C)	$V_{R2x}$ (m/min)	$V_{R3x}$ (m/min)	$V_{R4x}$ (m/min)
Engage-1	137	1	7.2	28.56	2.64	342	80	358	370	379
Engage-2	68	2	"	"	"	169	"	179	361	367
Engage-3	45	3	"	"	"	113	"	119	369	"
Engage-4.5	30	4.5	"	"	"	73	90	80	361	"
Aspun-4	23	4	"	"	5.27	116	"	122	489	498
Aspun-4.75	20	4.75	"	"	"	98	"	104	"	"

The diameter of the produced fibres is controlled by the draw ratio through the entire system,  $V_0$ /Winder speed. This draw ratio and the volume ratio were kept constant to get fibres with comparable geometry. Figure 10 below shows a bi-component fibre with ASPUN + 10 wt% CB as core material and PVDF as sheath material with SSDR 4 which is the same fibres used for piezoelectric testing.

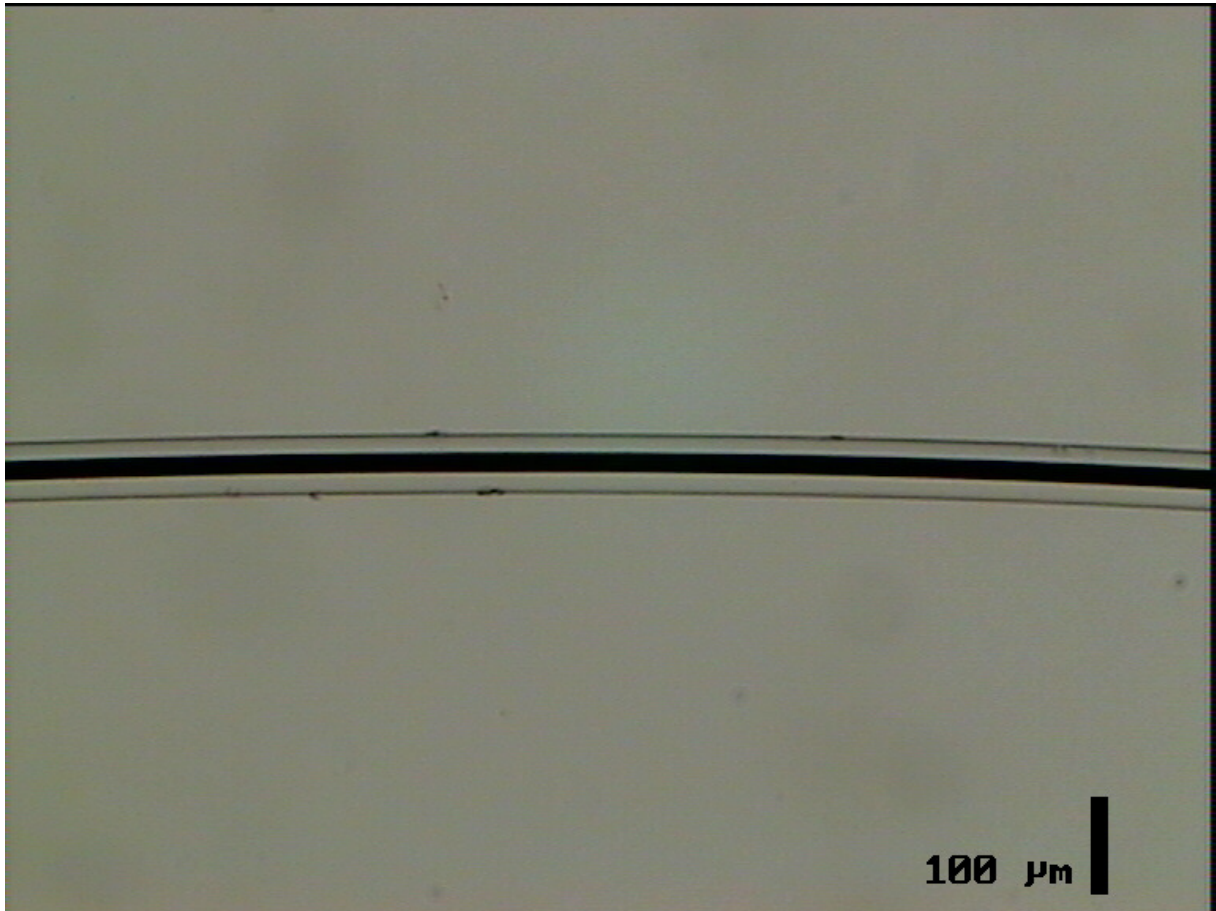


Figure 10. Bi-component fibre consisting of Aspun with 10 wt-% CB (Black) and PVDF (Transparent). Approximately 70 $\mu\text{m}$  in diameter with a core around 24 $\mu\text{m}$  and a sheath thickness of about 23 $\mu\text{m}$ . Picture taken with a Nikon SMZ1500 light microscope.

### XRD

XRD was used to measure alpha to beta-phase conversion in fibres with different SSDR. The choice to use XRD to confirm beta-phase development is based on earlier work at Swerea IVF (3) where PVDF fibres with different SSDR were investigated with XRD. The alpha-phase has three peaks at  $2\theta=26.5$ ,  $27.6$  and  $30.0^\circ$  while beta-phase PVDF have one peak at  $31.0^\circ$ .

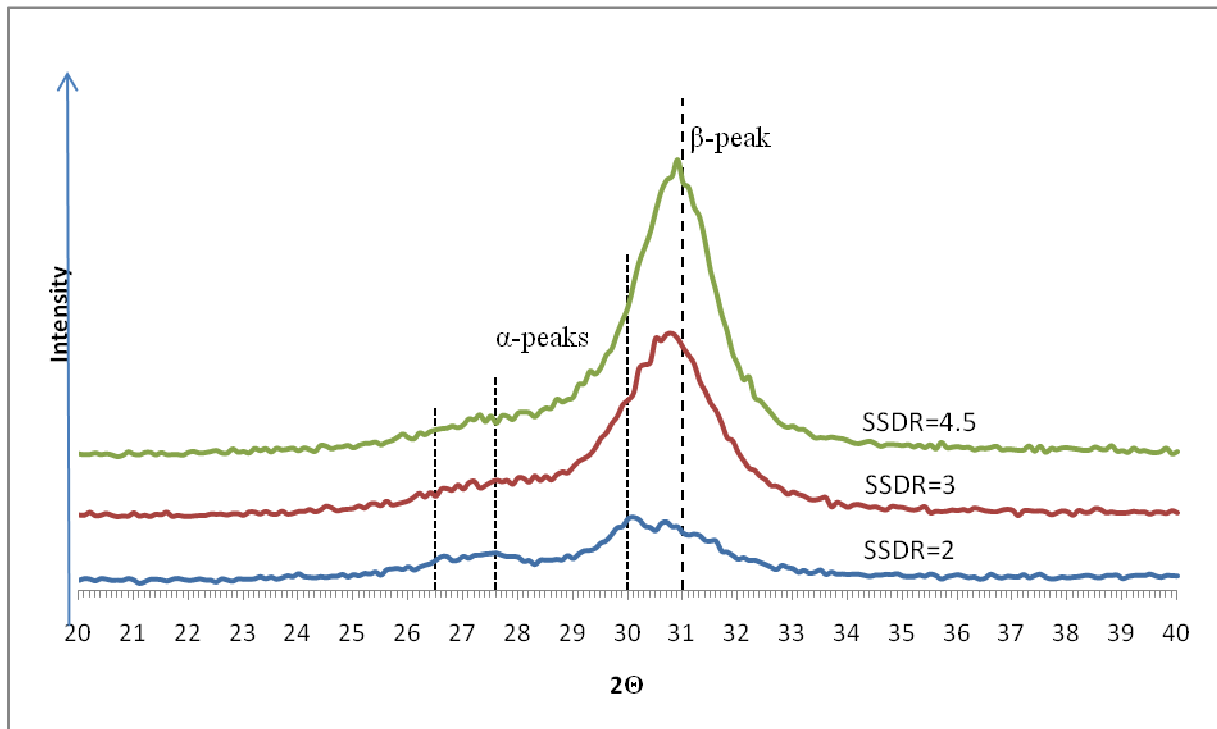


Figure11 . X-ray diffractograms of PVDF/Engage+10 wt-% CB bi-component fibres spun with SSSR=2, 3 and 4.5. The sheath/core ratio was 12/3. The curves were shifted along the intensity axis for better clarity.

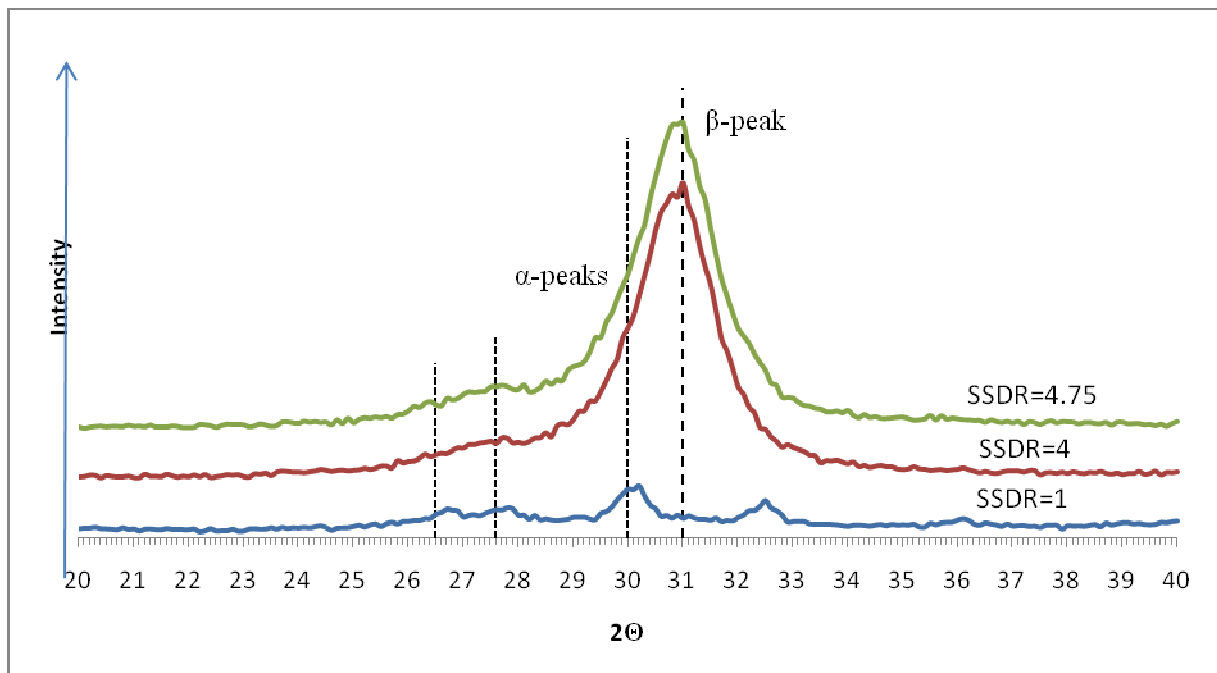


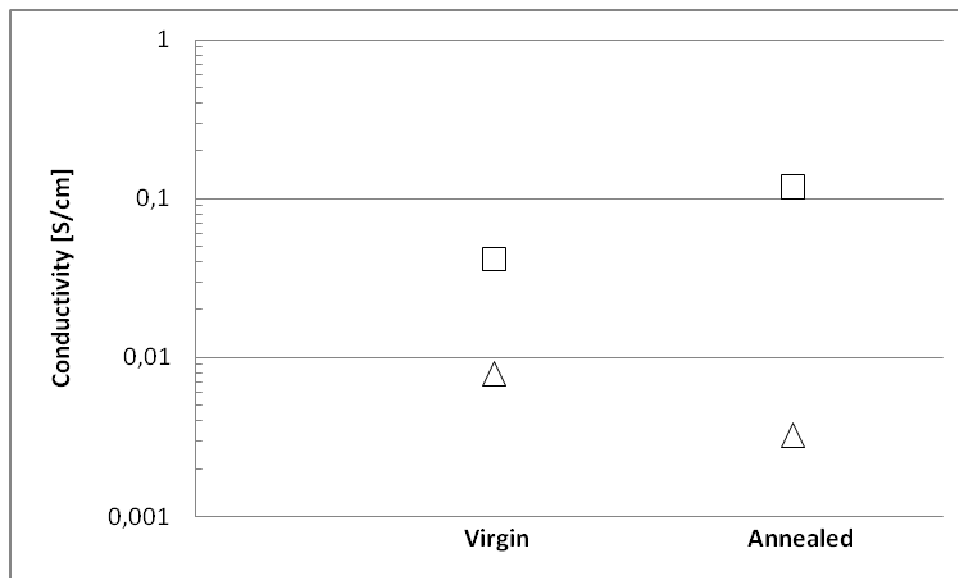
Figure 12. X-ray diffractograms of PVDF/Aspun+10 wt-% CB bi-component fibres spun with SSSR=4.0 and 4.6 (Sheath/core ratio 12/3). The lower curve was measured on un-drawn filaments (Sheath/core ratio 10/6). The curves were shifted along the intensity axis for better clarity.

In Figure 11 XRD results for ENGAGE yarns with SSSR=2, 3 and 4.5 are presented. It appears to be a gradual transition from  $\alpha$ - to  $\beta$ -phase PVDF as the SSSR increases. In figure 12 XRD results for ASPUN yarns with SSSR=4 and 4.75 is presented together with a curve measured on un-drawn filaments. The un-drawn filaments show three peaks typical for PVDF  $\alpha$ -phase while SSSR=4.0 and 4.75 produces a

dominant peak around  $31^\circ$  typical for the  $\beta$ -phase and there is little difference between SDR 4 and 4.75. The peak at  $2\Theta=32.5^\circ$  for the un-drawn filaments with sheath/core ratio 10/6 is probably related to the core material (PE or CB). This peak is hardly noticeable for the fibres with sheath/core ratio 12/3.

## Annealing

The electrical conductivity of the core material is significantly decreased by the spinning process, see Figure 13 compared to figure 8 and 9.



**Figure 13. Conductivity of the core material in bi-component PVDF/Engage+10 wt-% (Δ) and PVDF/Aspun+10wt-% (◻) fibres before and after annealing. SDR for PVDF/Engage+10 wt-% and PVDF/Aspun+10wt-% fibres were 4.5 and 4 respectively**

For the Aspun/CB composite the conductivity decreases from 0.22 (see Figure 9) to 0.04 S/cm, for Engage/CB the corresponding figures are 0.11 and 0.008 S/cm. The reason for the decrease in conductivity is believed to be the uni-axial drawing in the spinning process breaking conductive paths between the CB particles in the fibre direction. In an attempt to restore the conductivity after spinning the fibres were heat treated above the core materials melting temperature. As seen in Figure 13, annealing ENGAGE and ASPUN yarns gave different results regarding core material conductivity. Annealed ENGAGE yarns show a decrease in conductivity while annealed ASPUN yarns show an increase in conductivity, see figure 13. The temperature at which the yarns are solid state drawn is  $90^\circ\text{C}$  which is 10 degrees above the melting temperature of ENGAGE, this means that ENGAGE is annealed while drawn. Carbon black particles may attract each other in a polymer melt forming agglomerates (13). The space between agglomerates will increase as the agglomerates collect more and more carbon black particles. When the distance between agglomerates is big enough it is impossible for electrons to jump between them and that lowers conductivity. So it is possible that after annealing in an oven ENGAGE yarns is over-annealed and therefore conductivity decrease. ASPUN with a melt temperature of  $129^\circ\text{C}$  is not annealed at all during solid state drawing and therefore annealing these yarns have a positive effect on conductivity. It may also be speculated that the degree of molecular orientation in the core material may have a role in restoring conductivity upon annealing. The Aspun polymer is strongly oriented (drawn below the melting point) while the Engage polymer was drawn above its melting point. The relaxation processes during

annealing are thus much stronger in the case of Aspun and might affect the restoration of a conductive network of carbon particles.

### Piezoelectric measurement

The ASPUN yarns show higher conductivity than ENGAGE yarns at the same wt-% carbon black and are less temperature dependent because of the higher melt temperature. For these reasons the ASPUN yarn was selected for a piezoelectric response test. The ASPUN yarns with SDR=4 were chosen because the yarns at SDR=4.75 were at the absolute limit before spin line breakage (stable fibre production was not achieved) and the XRD show similar beta phase development.

The measurement was carried out at Chalmers University of Technology with a DMTA named RSA II. In Figures 14-16 the force signals from the DMTA are combined with the voltage signals from the fibres. The force signals from the DMTA is in volt where 1 volt = 1 Newton.

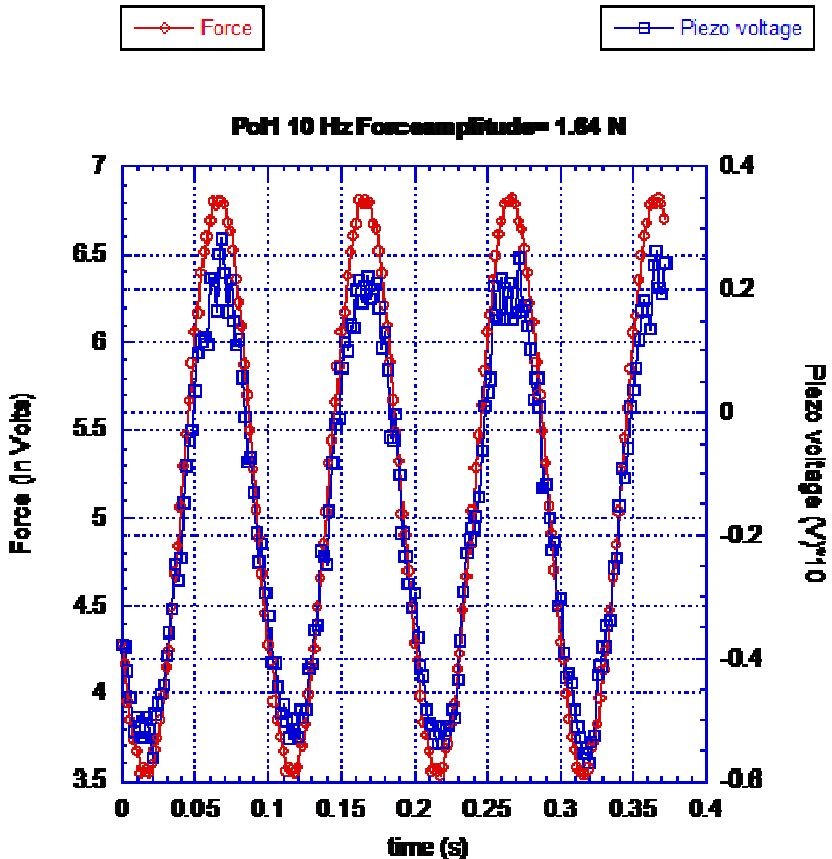


Figure 14. DMTA force output and piezoelectric volt output vs. time at 10Hz

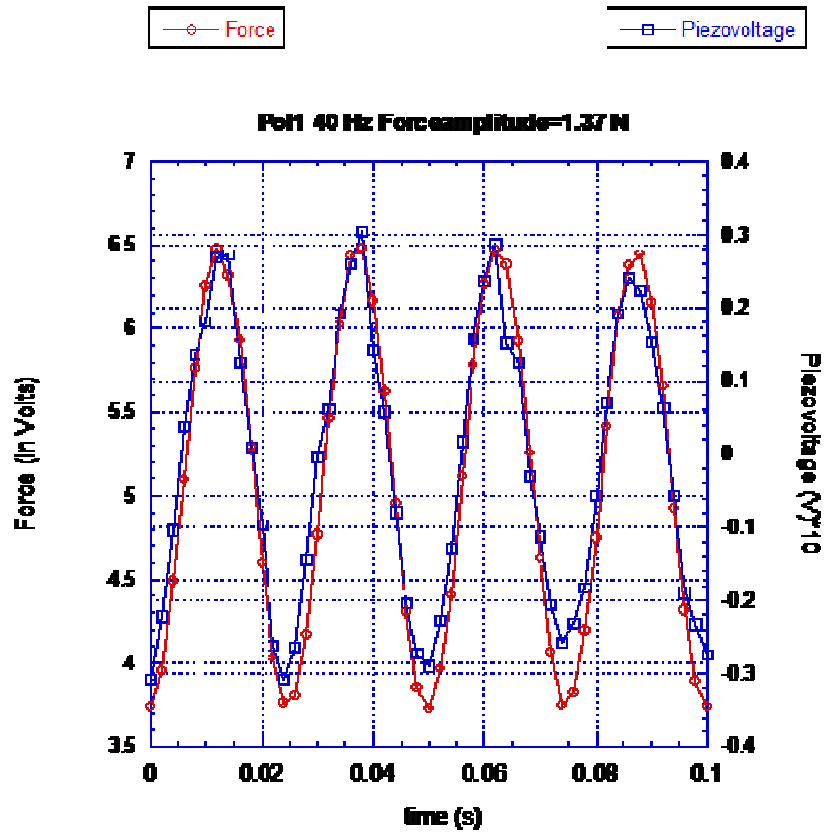
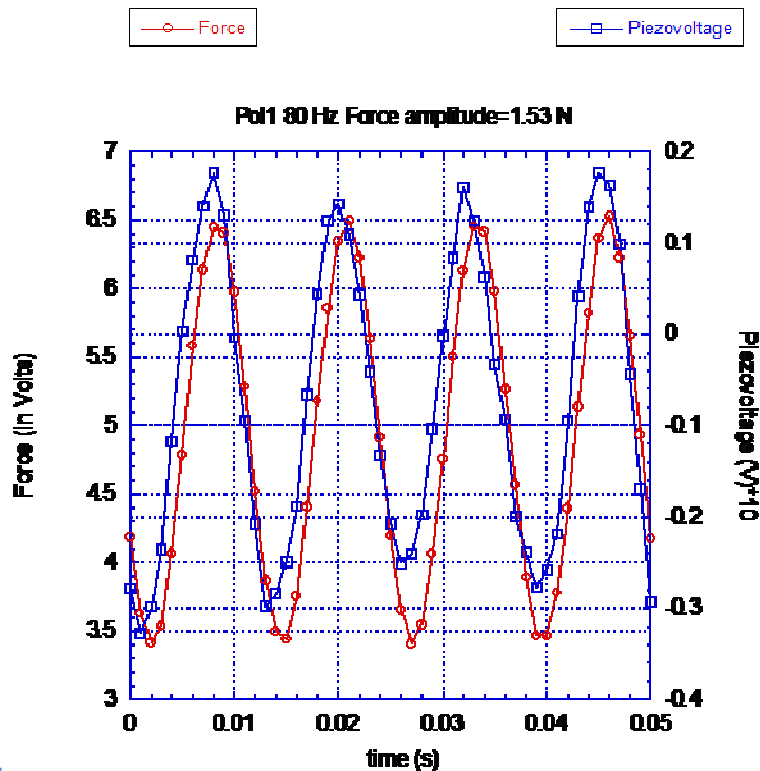


Figure 15. DMTA force output and piezoelectric volt output vs. time at



40Hz

Figure 16. DMTA force output and piezoelectric volt output vs. time at 80Hz

The figures show the force applied on the fibres from the RSAII and the voltage coming out from the fibres, amplified by a factor of 10, at different frequencies. As one can see the curves follow each

other proving that there is in fact piezo activity in the fibres. There is an increasing phase shift with increasing frequency. This could be due to the visco-elastic behavior of ENGAGE which is used as outer electrode. However, this need further investigations.

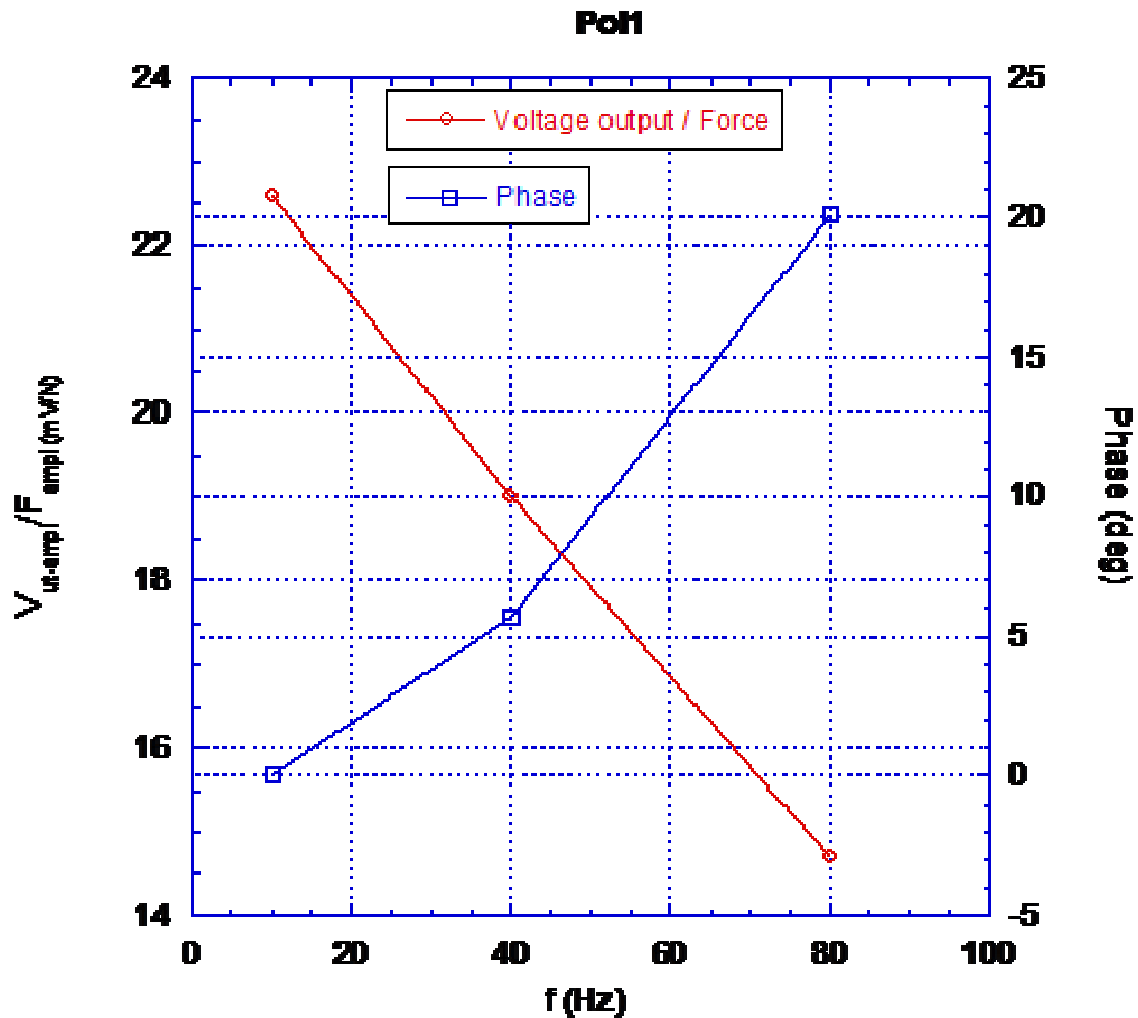


Figure 17. Output voltage / force and phase shift at different frequencies.

Figure 17 shows the output voltage/Force and the phase shift at different frequencies. At 10 Hz the fibres have an output voltage of 23mV/N which then decreases with increasing frequency. The reason for this behavior is not known at the time being.

The measured output voltage upon oscillatory stretching a fibre bundle is shown in Table 2.

Table 2. Piezoelectric respons in tension. The yarn used was Aspun-4, see Table 1. Filament diameter 70µm.

Sample	Poling Voltage (kV)	Linear density yarn (tex) (g/1000m)	Force amplitude (cN)	Frequency (Hz)	Peak-to-peak voltage (V)	Tension amplitude (cN/tex)	Volts per tension (V/cN/tex)	Nominal filament titer (tex) (g/1000 m)
1	1,8	886	250	5	5	0,3	18	4,0
1	1,8	886	500	5	10	0,6	18	4,0
1	1,8	886	1000	5	20	1,1	18	4,0
1	1,8	886	1500	5	30	1,7	18	4,0
2	1,75	829	1000	5	20	1,2	17	4,0
3	1,6	351	2000	5	60	5,7	11	4,0



The output voltage was found to be proportional to the applied force amplitude. By applying an oscillatory tensile load in the range of 0.25 - 2.5 kg at 5 Hz an oscillatory peak-to-peak voltage in the range 5 - 60 Volts was measured. The output voltage normalised to the “stress” in the fibres was in the range 10-18 Volts/cN/tex. The effect of poling voltage appears to be strong. However, the accuracy of the voltage reading during poling was relatively low and safe conclusions can not be drawn based on the limited data available.

Average fibre properties as measured by means of the Vibroscop/Vibrodyn tensile testing apparatus (Lenzing, Austria) are given in Table 3 and the corresponding tensile testing curves are reproduced in Figure 18.

Table 3. Measured mechanical properties of Aspun-4 fibres (see also Table 1).

Titer (dtex)	Tenacity (cN/tex)	Elongation (%)	Modulus (cN/tex)
38.65±4.09	24.8±1.7	60.7±10.4	181±12

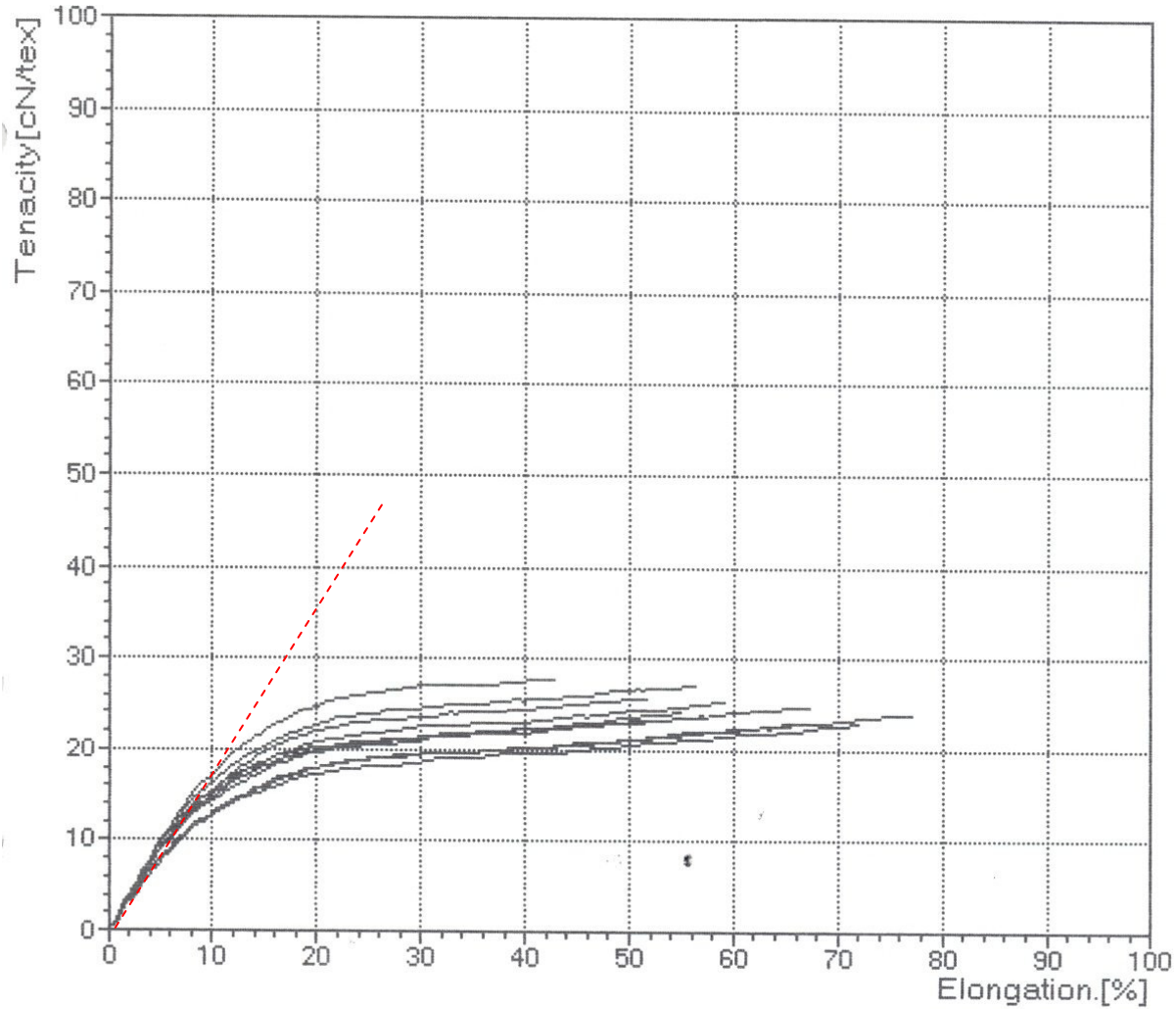


Figure 18. Tensile testing curves of Aspun-4 filaments. The dotted line corresponds to the E-modulus of 181 cN/tex.

The maximum tenacity applied during the tensile hand test was about 5.6 cN/tex which corresponds to a strain of about 3%. The force-elongation curve is linear at least up to about 10 cN/tex (6% strain). The tenacity-strain relation in the linear region is characterised by the E-modulus which is 181 cN/tex. In terms of strain the output signal was thus in the range 1800-3300 Volts per unit of tensile strain. A 1% strain would thus produce a voltage of about 18-33 V.

The figures in Table 2 should not be taken too literally since the force amplitude is estimated from a dynamometer in a simple hand test and may deviate by  $\pm 15\%$ .

Comparing the results from the tensile deformation with the "force sensor" case in lateral compression shows that the mode of deformation in the fibre is important. Stretching fibres produces a much higher effect compared to simply compressing the fibres in the radial direction. We also noted that a simple periodic bending of the fibre bundle resulted in an easy to measure periodic output voltage. It may be that much of the effect is canceled out in the case of the "force sensor" due to the state of stress developed in simple compression in the lateral direction.

## Conclusions

This work shows that it is possible to manufacture a piezoelectric fibre from PVDF homopolymer. The fibre properties are closer to normal textile fibres than ceramic fibres and can be truly integrated into textile materials.

The core material conductivity might not have that much impact on the piezoelectric testing as long as it is conductive but can be significant in specific applications. It is therefore concluded that annealing can help to increase conductivity in cold drawn fibres but can also decrease conductivity by means of over-annealing.

The output voltage from the fibres due to piezoelectric properties varies depending on how the testing is performed. The simple tensile test generates a higher output voltage compared to the “force sensor” test. This might be due to the internal structure in the force sensor where individual fibres are affected differently from the external pressure and as a result can cancel each other’s effect. However the force sensor was pooled in 1 kV and the tensile test fibres were pooled in 1.6 – 1.8 kV and as shown in table 2 the pooling voltage seems to have a strong effect on the output voltage from the fibres.

The piezoelectric effects measured is by all means high enough to promote continued research and development and seem to have potential in a number of applications including textile sensors, actuators and energy scavengers.

## Suggestions for further work

- Evaluation of piezo effect of single fibres in tension, bending and under hydrostatic pressure
- Explore three layer fibres with conductive polymer as core and outer sheath.
- Explore three layer fibres by applying a conductive coating on yarn level or fabric level
- Explore other methods than silver painting for contacting fibres (heat welding with conductive polymer composite, selective etching of core/sheath polymers with solvents)
- Improve conductivity by means of new/other polymer composites

## References

1. Zhang, Q.M., Vivek, Bharti and George, Kavarnos. *Poly(Vinylidene Fluoride) (PVDF) and its Copolymers*, John Wiley and Sons, Inc, 2002.
2. Measurement Specialties. 1000 Lucas Way, Hampton, VA 23666, USA
3. Lund, Anja. *Melt Spinning of Poly(vinylidene fluoride) Mono- and Bicomponent Fibres and Yarns - the Formation of Piezoelectric beta-phase Crystallinity*. Göteborg : Chalmers University of Technology, 2010. ISSN: 1652-8891.
4. Kawai, H. *The piezoelectricity of poly(vinylidene fluoride)*. 1969. pp. 975-976.
5. Mazurek, Boleslaw, Rozecki, Stanislaw and Kowalczyk, Dariusz. *Piezoelectric PVDF Cables*. Xi'an, China, 2000.
6. T.T, Wang and H, von Seggern. *High electric field poing of electroded Poly(vinylidene fluoride) at room temperature*. Bell Laboratories, Murray Hill, New Jersey 07974, 1983. Vol. 54.
7. J.E., McKinney, G.T., Davis and M.G., Broadhurst. *Plasma poling of poly(vinylidene fluoride): piezo- and pyroelectric response*. National Bureau of Standards, Washington, D.C. 20234, USA, 1979. Vol. 51.
8. Naohiro, Murayama. *Presistent Polarization in Poly(vinylidene Fluoride)*. Fukushima-ken, Japan 1975. Vol. 13.
9. Jan-Chang, Huang. *Carbon Black Filled Conducting Polymers and Polymer Blends*. Lowell, MA 01854, USA, 2002. Vol. 21.
10. Stauffer, D. *Introduction to percolation theory*. London : Taylor & Francis, 1985.
11. netzsch-thermal-analysis. [Online] [Quote: October 6 2010.] [http://www.netzsch-thermal-analysis.com/en/products/dma\\_dmta/](http://www.netzsch-thermal-analysis.com/en/products/dma_dmta/).
12. Strååt, Martin, Hagström, Bengt and Rigdahl, Mikael. *Conducting bicomponent fibres obtained by melt spinning of PA6 and polyolefins containing high amounts of carbonaceous fillers*. Submitted for publication in J. Appl. Pol. Sci.
13. Yihu, Song och Qiang, Zheng. *Influence of Annealing on Conduction of High-Density Polyethylene/Carbon Black Composite*. Hangzhou 310027, China, 2006. Vol. 105.