Continuous Production of Piezoelectric PVDF Fibre for E-Textile Applications

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Abstract. Polymers have been widely used as piezoelectric materials in the form of films and bulk materials but there are limited publications on piezoelectric fibre structures. In this paper the process of preparing piezoelectric Polyvinylidene Fluoride (PVDF) fibres from granules by continuous melt extrusion and in-line poling is reported for the first time. The poling of PVDF fibres was carried at an extension ratio of 4:1, temperature of 80 °C and high voltage of the order of 13000 V on a 0.5mm diameter fibre in a melt extruder. The entire process of making PVDF fibres from granules and poling them to make piezoelectric fibres was carried out in a continuous process using a customised melt extruder. The prepared piezoelectric fibres were then tested using an impact test rig to show the generation of voltage upon application of an impact load. PVDF granules, unpoled fibres and poled fibres were examined by Fourier Transform Infrared Spectroscopy (FTIR) which shows the presence of β phase in the poled fibres. The ultimate tensile stress and strain, Young's modulus and microstructures of poled and unpoled fibres were investigated using a scanning electron microscope (SEM).

1. Introduction

Piezoelectric polymer structures have been used for various applications ever since piezoelectricity was discovered in PVDF by Kawai [1] in 1969 . The availability of flexible polymer based piezoelectric materials has attracted several applications and studies. Most of the applications use either thick or thin films of PVDF [2–5] and some use bulk materials [6]. Due to the flexibility of the polymer materials various sensors and actuators have been developed using piezoelectric polymers. With a renewed interest in renewable energy generation and urgency to reduce the carbon foot print, energy harvesting from renewable resources and body motion has been widely studied using piezoelectric PVDF [2], [6], [7]. There is also a high demand for electronic textiles (e-textiles) or smart textiles that can be used in everyday garment for electrical or computing applications. One of the attempts to generate energy from human walking by Shenck *et al.* [6] by embedding a combination of piezoelectric PVDF and Lead Zirconate Titanate (PZT) structures in the shoe was successful to power a low energy electronic device. Another attempt to harvest energy from human body motion was by Granstrom *et al.* [8] where these

researchers embedded piezoelectric PVDF films into the straps of a backpack.

Li *et al*. [2] and Vatansever *et al*.[9] demonstrated that piezoelectric PVDF can be used to generate a continuous power of the order of 100 μW using wind energy at moderate wind speeds. Most of the earlier research reported that ceramic based piezoelectric structures generated higher voltage than the piezoelectric PVDF structures [10] [11]. Vatansever *et al*.[9] have recently demonstrated that under certain conditions such as generation of energy from the wind and rain, piezoelectric PVDF generated higher voltage and power compared to ceramic based PZT and Piezoelectric Fibre Composite (PFC) structures. One of the reason is due to the lower stiffness (low resonance frequency) of the PVDF structures. Piezoelectric polymer film dimension is restricted by the complexity of large scale production and poling process. The polymer film's mechanical properties are also less favourable for outdoor applications compared to a woven or knitted fabric of the same size. A piezoelectric fibre can be used to produce large fabrics which can be employed in energy harvesting applications from wind or rain. Egusa *et al*.[12] reported production of a multi-material fibre that was piezoelectric. However the multi-material and multi-process method where a copolymer of PVDF, P(VDF-TrFE) and polycarbonates are used makes the fibre expensive and difficult to scale up for large scale production.

In this paper, a low cost, single material and continuous process of producing a piezoelectric polymer (PVDF) fibre in a melt-extruder for the first time [13] is presented. The piezoelectric PVDF fibres were tested under an impact tester for voltage generation and the results are compared with the standard piezoelectric PVDF film. Microstructures of both poled and unpoled fibres are also compared and FTIR analyses of the poled fibre, unpoled fibre and PVDF granules of samples are carried out for comparison purposes

2. Experimental Details

2.1 Production of piezoelectric PVDF fibre

Production of piezoelectric PVDF fibre was carried using low viscosity Solef 1008 homo-polymer granules obtained from Solvay Plastics Ltd [14]. The polymer had a melting point of 172°C, glass transition temperature of -30°C and density of 1780 kg/m^3. The elongation at break value of the material was 50% at a draw rate of 50 mm/min at 23°C. A single screw laboratory line melt extruder originally constructed by Plasticisers Engineering UK was used for melt extrusion of the piezoelectric PVDF fibres. The extruder screw had a diameter of 22mm which can be operated at speeds of up to 50rpm though a reduction gear mechanism. The polymer was fed through the screw at a rate of 4g/min at 10rpm. The extrusion line had two water cooled slow rollers - four temperature controlled slow rollers and two fast rollers - that can draw the fibres at 15 m/min, 15 m/min and 100 m/min, respectively. The air blower below the extrusion die allowed air quenching of the fibre during extrusion.
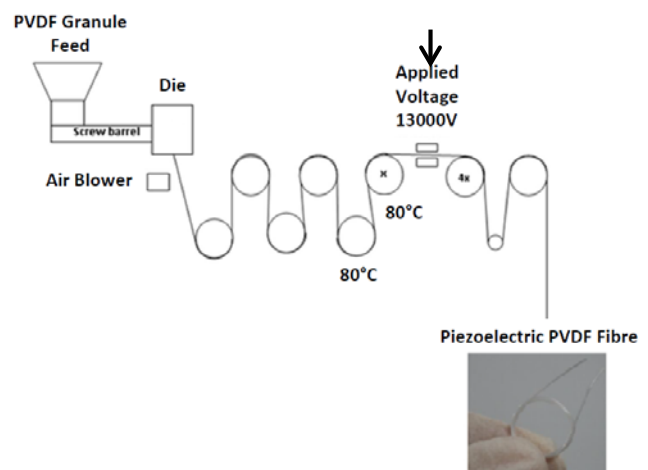

Fig. 1 Continuous process of making piezoelectric PVDF fibres using a custom melt extruder and high voltage power supply

PVDF granules were dried in the oven to remove any moisture and then fed into the feed screw

gradually. The temperature was maintained at 10°C above the melting point of polymer of 172°C at the beginning of the screw, 20°C above the melting point of the polymer at the end of the feeding screw, and 30°C above the melting point of PVDF at the die where the fibre was extruded. The extruded fibre was then air cooled with a blower as shown in Fig. 1. The water cooled rollers were used for additional cooling of the fibre and temperature controlled rollers heated the fibre to the poling temperature. The space between temperature controlled slow rollers and the fast rollers housed two plate electrodes separated by 10 mm gap. The arrow indicates the direction of the applied poling field which is radial to the fibre. The electrodes were connected to a Spellman SL300 series high voltage power supply with a range of 0-20kV at an output current of 3mA. The fast rollers' speed was maintained at four times that of the temperature controlled slow rollers in order to obtain an extension ratio of 1:4. Poling conditions (temperature, extension and high voltage) were applied simultaneously on the fibre between the temperature controlled slow rollers and fast rollers as shown in Fig. 1. Both extrusion and poling of PVDF fibres was carried out in a single continuous process, called as in-line poling on an existing melt extruder line. In other studies reported in the literature the poling process was performed separately outside the extrusion process [15] [16].

2.2. Characterisation of piezoelectric fibres

2.2.1 Voltage response testing

The piezoelectric PVDF fibres were tested for their voltage response by placing several fibres adjacent to each other on a copper plate. Another copper plate was placed on top of the fibres without making contact with the bottom plate. The top and bottom copper plates act as two electrodes that collect the charge from the fibres. This

structure was placed in an impact test rig (Instron Dynatup® MiniTower®) that is uses ASTM D 3763 standard impact test method. A weight of 1.02kg was dropped from a height of 5cm as shown in Fig. 2. The voltage response from the structure was recorded using a digital oscilloscope. Similar structure was also constructed using conductive Indium Tin Oxide (ITO) coated polyethylene terephthalate (PET) film. Fig. 3 shows the voltage response of the poled fibres structure with copper electrodes and commercial piezoelectric film.
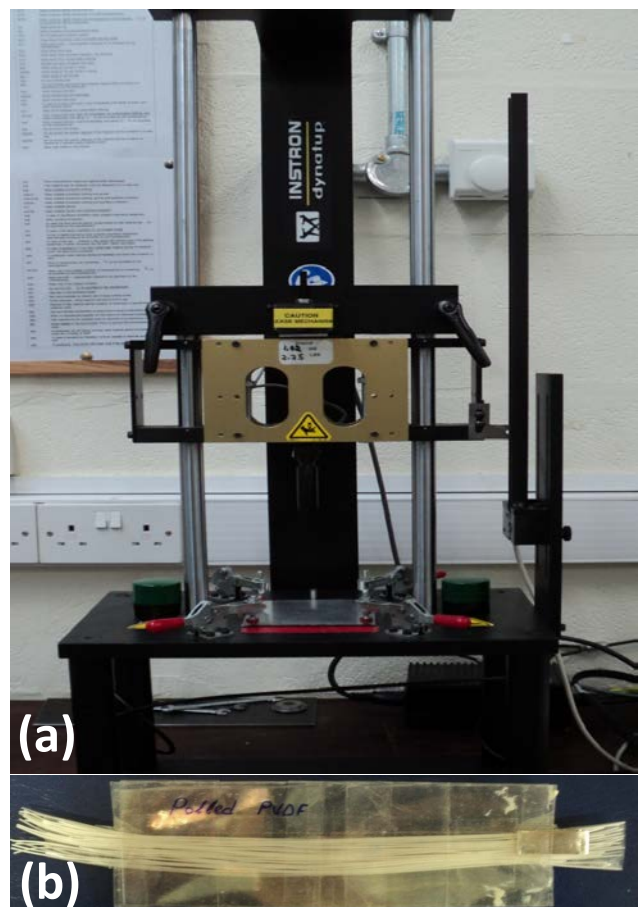

Fig. 2 (a) Impact test equipment where a weight of 1.02kg was dropped from a height of 5cm on both poled and unpoled fibre structures. **(b)** the test sample with Indium Tin Oxide (ITO) coated conductive polyethylene terephthalate (PET) film as electrodes

2.2.2 Examination of PVDF fibre microstructure

A Hitachi S-3400N Scanning Electron Microscope (SEM) which has resolution of up to 3.0nm at 30kV and 10nm at 3kV was used for examining the microstructure of PVDF fibres. The SEM used an accelerating voltage of 8kV using a tungsten filament. The microstructure images of poled and unpoled fibres were captured at various magnifications and compared. Fig. 4 (a) shows SEM image of poled fibre and (b) unpoled fibre.

2.2.3 FTIR Analysis

Thermo Scientific's Nicolet 6700 FT-IR Spectrometer was used for recording the infrared spectra of granule, poled and unpoled fibre of PVDF. Smart iTR accessory was used along with the Nicolet 6700 FT-IR Spectrometer. Fig. 5 shows the FTIR spectrographs of the granule, unpoled and poled PVDF in absorption mode. OMNIC software was used to plot the absorption spectra as a function of wave numbers and combine the spectra of granule, unpoled and poled fibres of PVDF into one spectrograph.

3. Results and Discussion

The piezoelectric PVDF fibres were prepared by drawing the melt extruded fibre and subjecting it to high voltage at elevated temperature. The material's piezoelectric effect is directly related to the degree of polarization achieved. In order to induce polarization, the dipoles in PVDF must be reoriented through the application of a strong electric field at elevated temperature. The domains are locked in the polarised state by lowering the temperature in the presence of the electric field.

To test the poled PVDF fibres an impact tester was used to apply an impact force from a 1.02 kg mass falling from a height of 5 cm. Voltages generated by the PVDF fibres were collected by
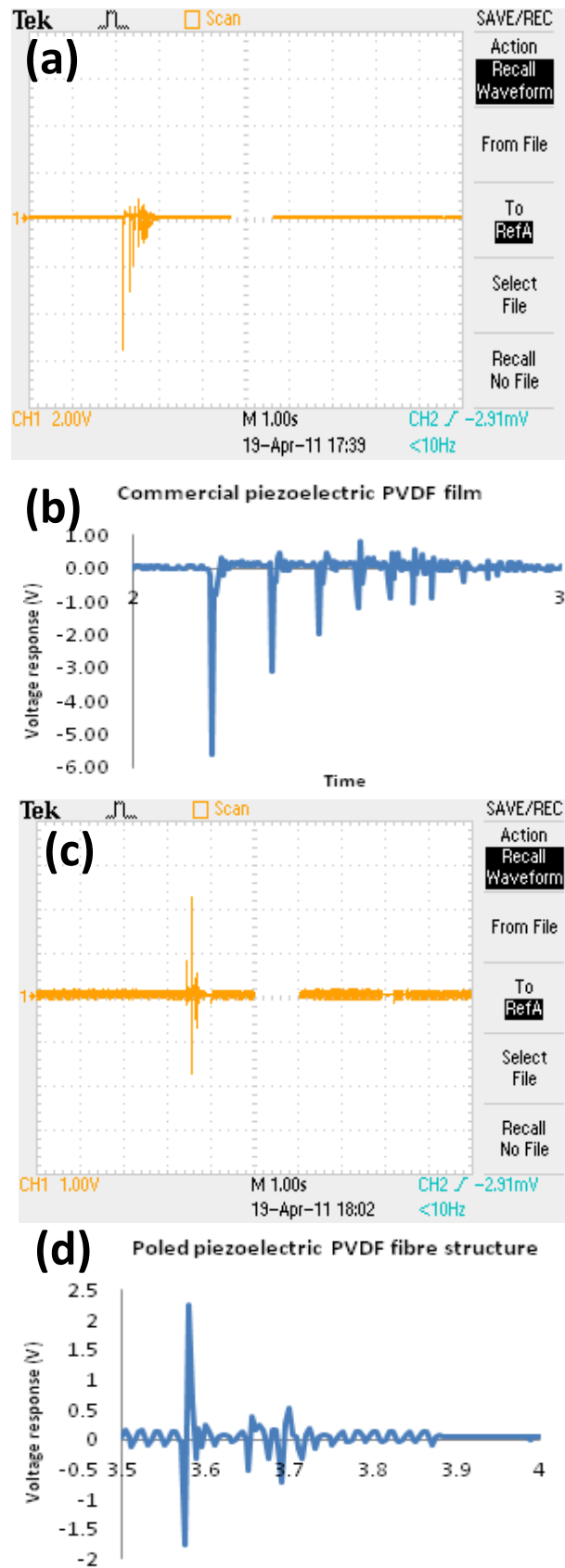

Fig. 3 Voltage response of **(a)** commercial piezoelectric PVDF film, **(b)** its magnified response **(c)** Voltage response of poled piezoelectric PVDF fibre structure upon an impact force, **(c)** its magnified response.

the electrode sheets on top and below acting as opposite charge collectors. Voltage was also recorded when a commercial piezoelectric PVDF film was tested in the impact tests keeping the height, dropped weight and the base support constant. Peak voltage generated by the fibre structure was approximately 2.2 V whilst that of the commercial piezoelectric film was 5.6 V as shown in Fig. 4 (a) and (b), respectively. It can be noted that the fibre structure produces both positive and negative voltages at different time intervals whilst piezoelectric film produces most of its voltage in one polarity. This suggests that the fibres were not firmly held in the structure hence, they vibrate upon impact giving rise to voltage generation in both negative and positive polarities.
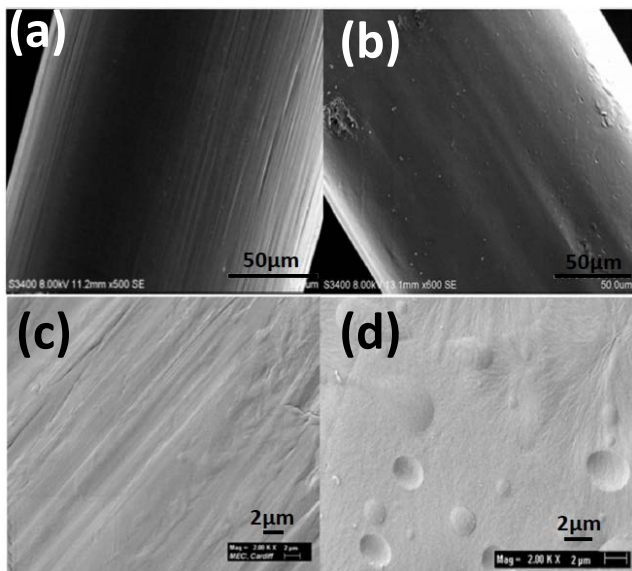

Fig.4 SEM image of PVDF fibre surfaces: **(a)** unpoled fibre surface at a low magnification of 600x indicating straight lines **(b)** poled fibre surface at a low magnification of 600x indicating small holes **(c)** surface of unpoled fibre at higher magnification of 2000x indicating straight lines **(d)** surface of poled fibre at higher magnification of 2000x indicating small holes.

The impact tests were carried out at various positions on the fibre structure and it was found that the voltage generated remains approximately the same for all the positions the structure. If the fibre polarity is taken into account while building the test specimen, the voltage generated by the fibre structure will be higher when all the fibres were aligned with all the positively charged sides on one sheet electrode and negatively charged sides on the other sheet electrode.

Swallow *et al.*[11] reported that in piezoelectric fibre composites (PFC) the distance between the fibres also affected the voltage generation and there is an optimum distance to diameter ratio between the fibres that leads to the highest voltage generation otherwise there will be arcing losses. Poled and unpoled PVDF fibres were investigated under SEM at various magnifications and on various locations of the fibres. The images shown in Fig. 5 (a) and (b) were selected having a magnification of 600 and were captured in vacuum with an accelerating voltage of 8000V and Fig. 5 (c) was captured with a magnification of 2000. The surface topography of the PVDF fibres, both poled and unpoled, can be clearly seen in the scanning electron microscope (SEM) micrographs. There are some obvious differences in the surface morphologies of the two fibres. The surface of the unpoled fibre appears to not to contain many voids whereas the poled fibre shows surface roughness in the form of enhanced pitting of the surface. A closer SEM analysis of the poled fibre shows the presence of voids of 2μm diameter all over the fibre surface (Figure 6c). A similar phenomenon has been observed by Lee *et al.* [17] who investigated surface morphology of metalized PVDF films using atomic force microscopy (AFM) and their results showed that under an external potential, the surface roughness was increased and under stress voltage output was generated. These workers also reported that the surface roughness of the PVDF film increased linearly with an increase in the poling voltage. A further morphological analysis of the fibre surface, using AFM or field emission scanning electron microscope, may reveal more significant variation in the microstructures of the unpoled and poled fibres investigated in our study.

The presence of β – phase in the poled and unpoled PVDF fibres was investigated by FTIR analysis, which allowed spectral measurements in the finger print region (500 – 1600 cm^{-1}) for different crystalline phases. Analyses were conducted on the poled fibre, unpoled fibre and granules of PVDF. Fig. 5 shows the absorbance spectra as a function of wavelength. Red spectra are from the poled PVDF fibres, green spectra are from the unpoled PVDF fibres and blue spectra are from the granules of PVDF. It can be seen from the spectra that the unpoled fibre and granule have distinct peaks at wave numbers 975cm^{-1}, 795 cm^{-1}, 765 cm^{-1}, 615 cm^{-1} and 530 cm^{-1}. These peaks represent α phase of PVDF which are not present at the same intensity level in the poled PVDF fibres. Peaks at wave numbers 840 cm^{-1} and 600 cm^{-1} are present in all the three materials (poled fibres, unpoled fibres and granules of PVDF). These peaks represent β phase of PVDF and are present in all the 3 forms of PVDF samples suggesting that poled PVDF has major composition of β phase and some β phase is also present in the unpoled and granular PVDF which is in agreement with previously reported work on FTIR studies of poled and unpoled PVDF films[18–20].
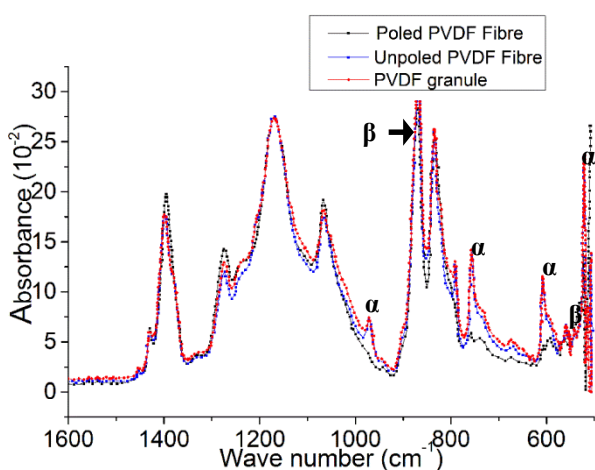
The presence of β phase in the unpoled fibre may be due to the tensile stresses and high temperatures that are applied during the normal extrusion process. PVDF granule also show the presence of both α and β phases but the volume fraction of the β phase which is responsible for piezoelectric effect is higher in poled samples followed by unpoled samples and the granules that is clearly evident in the XRD measurement shown in Fig. 6. Higher the stretch ratio during the extrusion of the fibre, higher is the intensity of the β phase indicating higher volume fraction of the piezoelectric β phase.
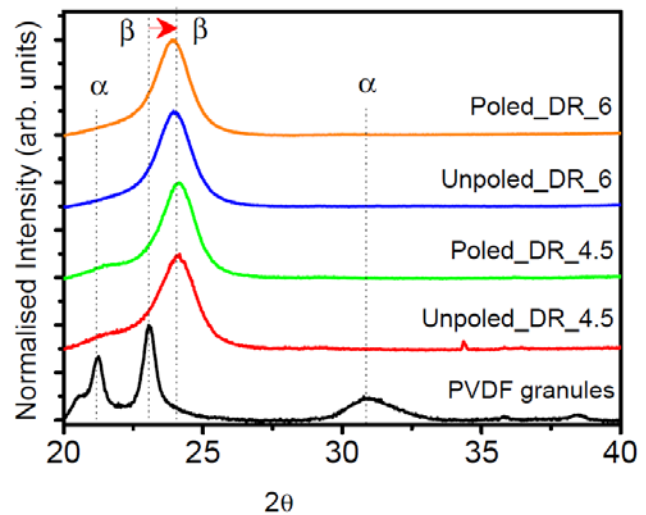

Fig. 6 XRD data (normalise intensity vs. 2θ) for poled fibres, unpoled fibres, and granules. It can be seen that the granules show the presence of both α and β phases but the β phase is shifted by about 1°.

The tensile properties of materials are of particular significance as they determine the suitability of the material in many applications. Various processes have a significant influence on the tensile properties of fibres via the morphological changes that are brought about by the process parameters. The effect of drawing and poling on the tensile properties of PVDF fibres was investigated in this work. Fig. 7 shows the stress–strain curves for the unpoled and ploed PVDF fibres. No significant differences were observed in the ultimate tensile stress and strain. However, a

Fig. 5 FTIR measurement of unpoled PVDF granule (red), unpoled PVDF fibre (blue) and poled PVDF fibre (black).

closer look at these results show that the unpoled PVDF fibres had an ultimate tensile stress of about 22 cN/Tex (391.6 MPa, based on the conversion of 1cN/Tex=$10\rho_f$ MPa where ρ_f is specific gravity) [21] an ultimate tensile strain of 59% whereas the poled (piezoelectric) PVDF fibres had an ultimate tensile stress of 25 cN/Tex (445 MPa) and an ultimate tensile strain of 55%.
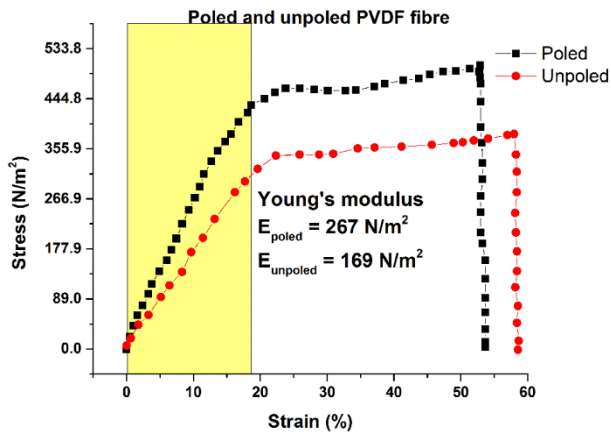

Fig. 7 Mechanical properties of PVDF fibres using Textechno Statimat M tensile test equipment. Stress vs. strain curve of unpoled fibres and poled fibres [22]

Average Young's modulus was calculated from the stress strain curve in the shaded regions where the stress vs. strain relationship is approximately linear. Young's modulus for poled and unpoled fibres was 15cN/Tex (267 MPa) and 9.5cN/Tex (169.1 MPa) respectively.Sencadas *et al.* [23] have concluded from their study that PVDF poled film exhibits superior mechanical properties than the unpoled film. They have proposed that this is fundamentally due to the morphological organisation of the ferroelectric polymer i.e. the enhanced orientation in the interphase region between the crystalline and the non-crystalline phases.

A more significance increase in the mechanical properties of the film in the longitudinal direction was observed. Gomes et al have studied the effect of stretching ratio and temperature on α to β phase

transformation in PVDF [24]. They observed that variations in the phase content are accompanied by changes in the degree of crystallinity and the microstructure of the material, and these changes had a significant impact on the macroscopic piezoelectric and ferroelectric response of the material. In another study reported that the morphological organization of the ferroelectric polymer plays an important role in its thermo-mechanical properties [25]. Lovinger noticed that PVDF is composed of small crystallites with typical dimensions of 10 nm, which are organised in groups of lamellae, with partially oriented amorphous intra lamellar phase. Thus it may be argued that the less organized structure that exists in the unpoled PVDF film will give rise to inferior mechanical performance of the material. The results of our study indicate that the poled fibres have somewhat superior mechanical properties than its unpoled counterpart, which is in agreement with the findings of the other studies on piezoelectric PVDF [23–25]

4. Conclusion

With the availability of inexpensive PVDF polymer and commercial energy optimisation electronics, it is now possible to make inexpensive energy harvesting devices however they are limited by the inability to produce them economically on large scale due to the multistage production and poling processes currently used. In this work we have extruded and poled PVDF fibres in a single continuous process on a standard melt-extruder and the process is easy to scale up. Piezoelectric fibres were tested under an impact force of 1.02kg dropped from a height of 5cm which generated a voltage of 2.2V which was lower than the commercial piezoelectric PVDF films. The poled and unpoled PVDF fibres were observed under an SEM and they were found to show some variation in the microstructure which suggests that they will exhibit some variation in

mechanical properties of the fibres. FTIR analysis shows the presence of larger amounts of β phase and lower amounts of α phase in the poled fibres. Converse is the case for the unpoled fibres. Our voltage generation results also confirm the presence of β phase in the poled PVDF fibre.

This process for the production of piezoelectric PVDF fibres in a continuous manner can provide a needed stimulus for large scale production of the material for energy harvesting textiles. These fibres are expected to be more economical and stronger than the piezoelectric PVDF films currently used. The energy conversion applications of the piezoelectric fibres developed in this study can be extended from wind and rain regeneration to waves and tides regeneration.

Acknowledgments

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