

HIGH PERFORMANCE MULTIMATERIAL FIBERS AND DEVICES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE
IN
MATERIALS SCIENCE AND NANOTECHNOLOGY

By
Mehmet Girayhan Say
June, 2016

HIGH PERFORMANCE MULTIMATERIAL FIBERS AND DEVICES

By Mehmet Girayhan SAY

June, 2016

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a dissertation for the degree of Master of Science.

Mehmet Bayındır (Advisor)

Fatih Büyükserin

Mehmet Z. Baykara

Approved for the Graduate School of Engineering and Science:

Levent Onural

Director of the Graduate School

ABSTRACT

HIGH PERFORMANCE MULTIMATERIAL FIBERS AND DEVICES

Mehmet Girayhan Say

M.S. in Materials Science and Nanotechnology

Supervisor: Mehmet Bayındır

June, 2016

Fabricating low energy requiring and self-powered flexible electronic devices can decrease world energy need since energy demand seems to be one of the most fundamental problems in the near future. An excellent solution to overcome this drawback is fabricating functional and energy efficient materials. Fabricating high piezoelectric coefficient materials that are compatible with mass production, easy to produce, low cost and non-toxic is highly demanded in order to design highly sensitive sensors and self-powered devices. This thesis introduces piezoelectric polymer (PVDF-TrFE) based several sensor types, energy harvesting devices such as; prosthetic hand, cardiac sensors, electronic skin, which represent promising device architectures for flexible electronics. Semiconductor, metal, composite, piezoelectric materials or polymers can be drawn by thermal fiber drawing and by applying iterative size reduction technique, the geometry, size and length of fabricated structures can be controlled, which also enables us to design novel in fiber, fiber-array devices at nanoscale. First, to enhance PVDF-TrFE fiber performance, crystallinity of fibers was improved by introducing new designs and phase transition mechanism was investigated in fabricated films and fibers. Finally, conductive composite material for flexible interconnects and electrodes was developed. As a whole, a variety of novel piezoelectric and conductive composite fibers were fabricated by using novel size reduction technique and fiber devices were designed for flexible electronics applications.

Keywords: Piezoelectricity, PVDF-TrFE, Polymer fiber drawing, E-skin, Conductive composites.

ÖZET

YÜKSEK PERFORMANSLI ÇOKLU-MALZEMELİ FİBERLER VE CİHAZLAR

Mehmet Girayhan Say

Malzeme Bilimi ve Nanoteknoloji Yüksek Lisans Tezi

Danışman: Mehmet Bayındır

Haziran, 2016

Enerji ihtiyacı yakın geleceğimizin en önemli problemlerinde biri olarak görülüp, düşük enerji sarf eden ve kendi enerjisini kendi üreten esnek elektronik cihazlar dünyanın enerji ihtiyacını azaltabilir. Bu sorunun üstesinden gelmek için fonksiyonel ve enerji verimli malzemeler çözüm olarak sunulmaktadır. Seri üretimle uyumlu, kolay üretebilen, ucuz ve toksik olmayan, yüksek piezoelektrik sabite sahip malzemeler üretmek, hassas sensör ve kendi enerjisini üreten cihazlar tasarlamak amacıyla yüksek talep görmektedir. Bu tezde piezoelektrik polimer (PVDF-TrFE) tabanlı, protez el, kardiyak sensörü ve yapay (elektronik) deri gibi çeşitli sensor tipleri ve enerji üreten/depolayan cihazlar, esneyebilen elektronik için gelecek vaat eden cihaz yapıları gösterilmiştir. Yarı-iletken, metal, kompozit, piezoelektrik malzemeler ve polimerler fiber çekme yöntemiyle üretilebilir olup, ardışık boyut küçültme tekniği ile bu malzemelerin geometrileri, boyutları ve uzunlukları kontrol edilebilir ve bu teknik özgün, fiber içinde ve fiber-dizi cihazları nano boyutta tasarlamamızı sağlar. Bu tezde öncelikle, PVDF-TrFE fiber performansını arttırmak için yeni tasarımlar ortaya koyarak fiberlerin kristal yapısı artırıldı ve faz geçiş sistemi incelendi. Son olarak, esnek iletken elektronik bağlar ve elektrot uygulamaları için iletken kompozit malzeme üretildi. Sonuç olarak, özgün piezoelektrik ve kompozit fiberler ardışık boyut küçültme tekniği kullanılarak üretildi ve esnek elektronik uygulamaları için fiber cihazlar tasarlandı.

Anahtar Kelimeler: Piezoelektrik, PVDF-TrFE, Polimer fiber çekme, E-deri, İletken kompozitler.

Acknowledgement

I would like to thank my academic advisor, Prof. Mehmet Bayındır for his support and guidance throughout my thesis. I am appreciative for his support and for letting me to research freely, for providing a collaborative atmosphere to join projects and independent research environment.

I would like to thank Mehmet Kanık and Murat Dere for all the support they have provided me through this journey. In fact they were not only friends and teammates to me, but also mentors. I would like to thank my friends and teammates; Bihter Dağlar, Mustafa Ürel and Alp Emre Acar. I had a wonderful time working with them. I am grateful to Prof. Hasan Tarık Baytekin and Prof. Aykutlu Dana for their suggestions and invaluable comments that improved the quality of my research.

I want to express my sincere gratitude to my friends who helped steer the wheel with me all the time and reach out to me whenever I need their assistance. I am grateful to Gökçen Birlik Demirel and Neşe Özgür for their friendship and assistance, also special thanks to Ahmet Faruk Yavuz, Gökçe Çelik, Muhammed Yunusa, Pınar Beyazkılıç, Abubakar Isa Adamu, Ersin Hüseyinoğlu, Gökhan Bakan, Abba Usman Saleh, Umar Musa Gishiwa, Ahmet Emin Topal, Hasan Güner, Murat Serhatlıoğlu, Seda Kizir, Bekir Türedi, Merve Marçali, Enes Palaz, Arda Okan and Mert Mermerci.

I had a good time and enjoyed sharing ideas with Bayındır research group members. They were the reason I felt comfortable to conduct my research in a conducive environment. I want to thank Fahri Emre Öztürk, Tural Khudiyev, Ozan Aktaş, Erol Özgür, Urandelger Tuvshindor, Osama Tobail, Mostafa El-Ashry, Dilara Oksüz, Pelin Tören, Orhan Genç, Arbab M. Toufiq, Ahmet Kağan Kolsuz, Reha Özalp, Ahmet Başaran.



To my family

Contents

Chapter 1 Introduction.....	16
1.1. Piezoelectricity	17
1.1.1. Piezoelectric Effect.....	18
1.1.2. Constitutive Equations	19
1.2. Carbon Nanotubes	22
Chapter 2 High Performance Piezoelectric Sensors and Devices.....	27
2.1. Introduction	28
2.2. Nanostructured Piezoelectric Polymers.....	31
2.3. Large Area Artificial Skin.....	36
2.3.1. Fabrication.....	36
2.3.2. Characterization.....	39
2.4. Cardiac Sensor.....	41
2.4.1. Fabrication.....	42
2.4.2. Characterization.....	42
2.5. Model Hand with Pressure Sensors.....	44
2.5.1. Fabrication.....	44
2.5.2. Characterization.....	47
2.6. Controlling the Piezoelectricity.....	49
Chapter 3 Highly Crystalline Piezoelectric Fibers.....	53
3.1. New Designs to Enhance Piezoelectricity.....	54
3.2. Fabrication of High Performance PVDF-TrFE Fibers	54
3.2.1. Preparation of Piezoelectric Film	54

3.2.2. Preform Design.....	55
3.2.3. Fiber Drawing.....	58
3.3. Material Characterization	60
3.3.1. XRD Phase Characterization.....	60
3.3.2. FTIR Characterization.....	62
3.3.3. Morphological Characterization.....	63
3.4. Iterative Fiber Drawing	65
Chapter 4 Conductive Polymer/Carbon Nanotube Composite Film and Fibers	68
4.1. Introduction	69
4.2. Material Characterization	71
4.2.1. CNT Characterization.....	71
4.2.2. Conductive Polymer Characterization.....	72
4.3. CPE/CNT Blend Fabrication and Characterization.....	74
4.4. Electrical Characterization	78
4.5. Fiber Design and Characterization	79
4.5.1. Preform Design.....	80
4.5.2. Fiber Fabrication	81
4.5.3. Fiber Characterization	83
Chapter 5 Conclusions.....	85
5.1. Conclusions	85
Bibliography	87

List of Figures

Figure 1: Direct and Converse effect. a) Permanent polarization after poling process. b,c) Compression or tension along the direction of polarization results a voltage same or opposite direction of the poling voltage (Direct piezoelectric effect). d,e) If a voltage of the same polarity or opposite polarity that of poling voltage is enforced , the element will get longer or shorter, respectively.....	18
Figure 2: Poling process. Initially dipoles are oriented randomly. Applying huge electric field domains are oriented. After DC field is removed, remnant polarization is obtained.....	19
Figure 3: Polarizing directions and effects of E field for polarizing mechanism. a) Typical curve of change in the polarization with electrical field. b,c) Direction of forces on a piezo element. Indirect or direct polarization can be characterized by polarization hysteresis.....	20
Figure 4: Applications of Piezoelectricity	21
Figure 5: Representation of SWCNT (a) and MWCNT (b).....	23
Figure 6: Illustration of conceptual construction of a honeycomb lattice. OCBA is a typical 1D unit cell for SWCNT. Zigzag and armchair structures in CNT lattice.....	24
Figure 7: Adopted from [48]. Three types of SWCNT: a) chiral, b) armchair, c) zigzag CNT.....	25
Figure 8: Schematic representation of two wire devices and types of electron transportation. a) A quantum wire between two contacts. b) SWCNT between two contacts. c) Illustration of electron scattering. d) Illustration of ballistic transport where an electron travels with a constant energy and momentum.	26
Figure 9: Schematic of human skin with various mechanoreceptors. Mechanoreceptors for receiving tactile information. Adopted from [57] and [58]......	29
Figure 10: Examples of pressure sensitive electronic skins, model hands and sensors. a) [62], b) [59] f) [68], g) [53].....	31

Figure 11: Optical and SEM images of 1st step and 2nd step P(vdf-trfe) Fibers. A) Cross sectional image of the first step PVTF microfiber in the PES cladding. B) Photograph of etched P(vdf-trfe) nanoribbons. C) SEM image of second step nanoribbons. D) Optical image of etched fibers for large area applications.....	35
Figure 12: Optical images of 1st step extracted piezoelectric fibers and 2nd step etched nanoribbons. A) First step P (vdf-trfe) fibers extracted out from the PES cladding. B) Optical image of the etched second step nanoribbons, Inset shows the fine fiber surface.	36
Figure 13: Fabrication steps for the artificial skin using second step fibers. a) Schematic representation of electrodes for large area e-skin device, word (W1-W10) and bit (B1-B10) lines are shown. b) Images of polymer masks for aluminum electrode fabrication, inset show the electrode schematic. c) Schematic illustration of artificial skin, materials and structures are shown. d) First layer of artificial skin with gold coated piezoelectric fibers, copper tapes and PDMS layer.....	38
Figure 14: Optical image of fabricated large area electronic skin. Optical images of first and second layer images of electronic skin with letter ‘B’. Bottom images demonstrate completed map transparency and flexibility.....	39
Figure 15: Electrical characterization of electronic skin. a) Optical image of experimental setup for the characterization of the piezoelectric device. b) Optical image of artificial skin with metal marble on W8 x B8 lines. c) 2D voltage signal intensity distribution measured from the 10 x10 e- skin matrix. Voltage mapping of the pressure distribution on W8xB8. d) Maximum open circuit voltage generated from the pressure that is applied by the marble.	40
Figure 16: Small pressure analysis of single pixel element of e-skin. Experimental setup for the small polymer drops on to the artificial skin surface. Images (1-3) shows the polymer mass fooling from the certain height. Data shows the maximum generated voltage by increasing pressure values. Inset shows the voltage peak for 9 Pa pressure value.	41
Figure 17: Schematic representation of cardiac sensors. a) Schematic of layers and device construction of piezoelectric nanowire electronic skin. b) Optical image of the designed cardiac device.....	42

Figure 18: Blood pressure measurements on the wrist, arm and neck. a) Open circuit voltage (V_{OC}) - time plot for a sensor placed on the wrist and photograph of the sensor on the wrist. b) V_{OC} - time plot for a sensor placed on the arm and photograph of the sensor on arm. c) V_{OC} - time plot for a sensor placed on the neck and photograph of the sensor on the wrist.....	43
Figure 19: Fabrication steps for the model hand with embedded pressure sensors. a) Optical image of 22 pressure sensors are prepared for embedding into the mold. b) Plaster mold preparation, inset optical images show mold and silicone hand design. c) First silicone pour out into the plaster mold and after sensors are placed onto the dried silicone layer. d) Embedded 22 piezoelectric sensors into the plaster mold with silicone.	45
Figure 20: Schematic representation of model hand. Pressure sensors with different diameters embedded into silicone rubber, inset shows the layers of each pressure sensor.	46
Figure 21: Optical images of model hand with sensors and wires. Photographs of labeled piezoelectric nanowire sensors with copper contacts embedded into silicone mold, the final structure is a model hand that can sense pressure values from various points.....	47
Figure 22: Electrical characterization of each pressure sensors in the model hand. a) Schematic representation for pressure actuation. b) Schematic representation of labeled 22 pressure sensors. c-f) V_{OC} release peaks of the sensors at full contact position.....	48
Figure 23: Mapping of a model hand for each pressure sensors. Open circuit voltage responses ranging from 50 – 100 V for piezoelectric sensors. Voltage mapping of pressure distributions for the mass.....	49
Figure 24: Molecular structure and phases of PVDF-TrFE. a) Molecular structure of the polymer that contains VDF and TrFE parts. b) Alpha phase demonstration of PVDF-TrFE. c) Beta phase demonstration of PVDF-TrFE).....	50
Figure 25: XRD analysis of treated and as-drawn fibers.	51

Figure 26: Electrical characterization of annealed and as-drawn fibers. a) Device structure. b) Voltage-time response of the fibers. c) Comparison of open circuit voltage values of the fiber devices.....	52
Figure 27: Surface topologies of first and second step annealed and as-drawn fibers. a,b,c) annealed and as-drawn fibers. d,e) Second step fiber surface topologies.....	52
Figure 28: Illustration of PVDF-TrFE polymer slabs that we produce by a directional press. a) Powder form of P(vdf-TrFE). b) Three pieces of Al mold. c) Hot pressed piezoelectric film.....	55
Figure 29: Fabrication steps for preform preparation. As an initial step, PES preform was fabricated that is a macroscopic copy of the cladding material (1). Inserting piezoelectric film into the PES solid (2). Final form of rectangular multi-material preform (3).....	57
Figure 30: PVDF-TrFE fiber production. a) Schematic representation of the thermal drawing of PES / PVDF-TrFE composite preform to obtain piezoelectric microribbons. b) Tens of meters of fiber samples. c) Scanning electron microscopy (SEM) images of cross-section of fibers. d) Macroscopic residual of the preform after thermal drawing process.	59
Figure 31: XRD analysis of all PVDF-TrFE powder form.....	60
Figure 32: XRD analysis of all PVDF-TrFE samples that were involved in fiber drawing process. XRD patterns of as-drawn and bulk film (a), Magnified image if XRD spectra at $2\theta=20^\circ$, which corresponds the piezoelectric beta phase (b), XRD patterns of annealed fibers that presents the degree of crystalline of the fibers, which are treated with different temperature values that correspond to the Curie (120°C) and melting (140°C) points of the piezoelectric material (c), XRD spectra of the preform that was left from the fiber drawing process, phase transition alpha to beta was represented (d).....	62
Figure 33: FTIR spectra analysis of the as-drawn, thermally annealed fibers and the bulk film under the light is polarized perpendicular to the direction of the fiber drawing. (a) FTIR spectra of the bulk film and the as-drawn fibers, beta phase is dominant. (b) FTIR spectra of the thermally treated fibers, beta phase is dominant.	63

Figure 34: SEM micrographs of PVDF-TrFE micro fibers produced by thermal fiber drawing. a) Cross-sectional of the piezoelectric fiber in the PES cladding. b) Magnified image of (a). c) Lateral image of extracted fiber. Inset: Etched fiber. d) Closer look at the microribbons that shows the piezoelectric film layers.	64
Figure 35: Schematic representation of iterative size reduction technique for PVDF-TrFE fibers.	65
Figure 36: Optical and SEM micrographs of PVDF-TrFE microribbons. a) Optical image of PVDF-TrFE microribbon array embedded in PES cladding. b) Optical image of second step PVDF-TrFE microribbons extracted out of their cladding. c-d) SEM images of second step fibers.	67
Figure 37: SEM images of the second step microribbons for morphological characterization. a) SEM images of arrays of PVDF-TrFE microribbons. b) Magnified image of the rectangular shape PVDF-TrFE fibers, approximately 2-4 μm in width. c) A closer look at the PVDF-TrFE microribbons that shows the crystallinity and the shape preservation of the material.	68
Figure 38: SEM and TEM images of MWCNTs. a) SEM image of MWCNT forest. b) SEM image of CNT bundles. c-d) TEM images of MWCNT.....	72
Figure 39: DSC and TGA analysis of CPE polymer	73
Figure 40: Mechanical characterization of CPE which corresponds the flexibility and stretchability of the conductive polymer.....	74
Figure 41: Schematic representation of MWCNT/CPE blends. Materials and film casting technique is represented.....	75
Figure 42: SEM images of CNT, conductive polymer and composite.a) SEM image of MWCNT. b) SEM image of conductive polymer. c-d) SEM images of MWCNT/CPE blends with different scale bars.....	76
Figure 43: Raman spectra of carbon loaded polyethylene (CPE)(a) ,unfilled CPE (b), second step composite fiber (c), 2 %wt composite film (d).....	77
Figure 44: Schematic representation and experimental setup images of four-point probe conductivity measurements.....	79
Figure 45: Schematic illustration of preform fabrication. The process starts with rod preparation (1,2), final form of preform (3). PC cover preform was prepared and	

CPE/CNT composite rod was prepared by additional consolidation. Finally, composite rod was inserted into the PC tube.....	81
Figure 46: Fabrication schematic of micro and nanowires. Iterative size reduction technique scheme allows us to achieve multimaterial nanometer size structures. A macroscopic composite rod was inserted into a PC tube. Tens of meters long composite microribbons were encapsulated in PC. First step fibers were stacked and redrawn in a new PC preform in order to decrease size of the ribbons down to nanometers. Further size reduction can be achieved by following restacking and redrawing cycles	82
Figure 47: Optical and SEM images of micro and nanowires for each drawing step. CPE/CNT composite microribbon images obtained by etching the PC cladding. Cross sectional image and macroscale image of first step fibers. SEM and optical images of both second step microwires and third step nanowires.	83
Figure 48: Alignment of micro and nanowires after applying iterative size reduction technique	84

List of Tables

Table 1: Table of structural parameters and equations for CNTs. cCNT stands for chiral CNT, aCNT for armchair CNT, zCNT for zigzag CNT	24
Table 2: Piezoelectric Properties of Nanostructured PVDF-TrFE Polymers Reported in the literature.	34



Chapter 1

Introduction

Electronic devices and systems that are established on flexible substrates have received great attention because silicon wafer technology has limited flexibility [1-7]. Organic solar cells, flexible displays and cameras, artificial skins were recently demonstrated on plastic flexible components such as substrates, circuit components, and electrodes [8-14]. Designing high performance and flexible devices such as e-skin and tactile devices, several materials technologies have been used, for example, triboelectric polymers, OFET technology, piezoelectric and pyroelectric materials, inorganic semiconductors, pressure sensitive nanomaterials and composites [15-21]. In addition to the materials for e-skin, sensors and artificial muscle, energy harvesting applications, there is still a huge need to develop piezoelectric and conductive composite materials that can pave the way for new functions and designs. [24-28]. Although conventional electronic and photonic materials are very efficient in terms of functionality and performance, integration of these materials as a part of a circuitry into a flexible, curved and stretchable substrate is not implemented easily. These requirements can be accomplished by soft electronic fiber devices, which are non-invasive, biocompatible, and highly stable [22, 23]. Semiconductor, conductive, composite, piezoelectric materials or polymers can be drawn by thermal fiber drawing and by applying iterative size reduction technique [23] the geometry, size and length of fabricated structures can be controlled, which also enables us to design novel fiber, fiber-array devices at nanoscale.

Recently Bayindir Group researchers have produced kilometers long, well-ordered, uniformly distributed piezoelectric poly (vinylidene fluoride) (PVDF) micro and nanoribbons that demonstrates spontaneous piezoelectricity [25]. These structures can be drawn thermally with Polyether Sulfone (PES) or Polycarbonate (PC) cladding, which encapsulates the inner, piezoelectric material. New efforts to enhance piezoelectricity in fibers, drive us to choose materials that have superior properties

such as, easy to produce, geometrically controlled, high piezoelectric coefficients, and crystal phase stability. To achieve these requirements poly vinylidene fluoride - trifluoroethylene (PVDF-TrFE) polymer has been selected as an excellent candidate for fabricating multi-material piezoelectric micro and nanostructures.

In this work, we designed and fabricated functional pressure sensitive devices from the PVDF-TrFE micro and nanowires that were fabricated by our group. To demonstrate fibers' device performance, several applications such as artificial skin, cardiac devices and model hand were designed, which are good examples of flexible electronic devices. All devices were fabricated by following common flexible device design structure: flexible substrate, piezoelectric polymer and flexible electrode, respectively. Typically, it is very important to fabricate highly crystalline piezoelectric materials that have high piezoelectric coefficients, therefore highly crystalline PVDF-TrFE microwires were fabricated and phase transition characterization were confirmed recently by our group. Additionally, conductive polymer/Carbon nanotube composite film was prepared and composite micro and nanowires were fabricated for flexible electrode applications.

1.1. Piezoelectricity

Piezoelectricity is a natural phenomenon that was observed by Pierre and Jacques Curie brothers in 1880s. In Greek, the word 'piezo' corresponds to press, which conveys energy generated from pressure where piezoelectric material demonstrates surface charges when they are mechanically disturbed. Piezoelectricity can be observed in many different materials such as ceramics, polymers and even biological substrates [29 - 31] also, various applications can be utilized in the field of sensing [32], actuation [33, 34], and energy harvesting [25, 35]. In order to design functional piezoelectric devices, there are several requirements need to be considered, for instance having high piezoelectric coefficient, flexibility, biocompatibility and easy to process [36]. Although ceramic based materials and composites are known to have high piezoelectric coefficients, they are depreciating in value from high production costs, toxicity, and high processing temperatures [37]. With the discovery of piezoelectric polymer PVDF [38], piezoelectric polymers become promising

candidates for the replacement of ceramic materials, because of their high piezoelectric coefficients, biocompatibility and flexibility [25, 39]. PVDF and its co-polymer PVDF-TrFE are known as efficient polymer piezoelectric materials, and can be fabricated in the forms of thin films or nanowires, which pave the way for high efficiency and functional devices [30, 40].

1.1.1. Piezoelectric Effect

Piezoelectric materials are different than other dielectrics the mechanical compression or tension changes the dipoles, these procedures generates voltage. There are two types of piezoelectric effect, namely, direct and converse piezoelectric effect (Figure 1). For direct piezoelectric case, applied force changes polarization and creates voltage on electrodes. When a potential is applied to both ends of the material, this changes the distance of crystal planes and results a variation in shape of the dielectric material. This effect is termed as converse (indirect) piezoelectric effect.

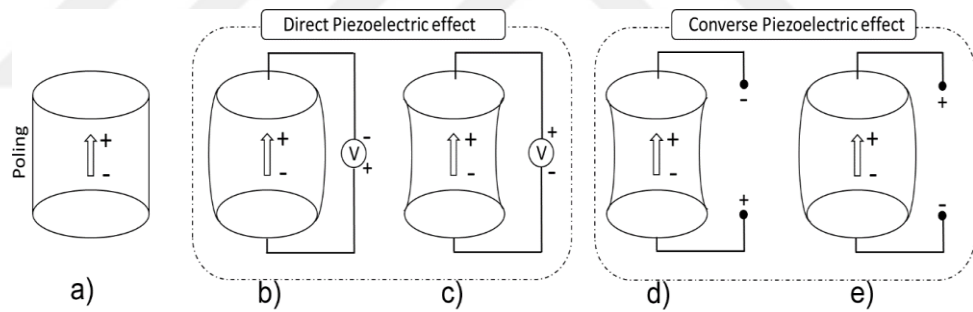


Figure 1. Direct and Converse effect. a) Permanent polarization after poling process. b,c) Compression or tension along the direction of polarization results in a voltage same or opposite direction of the poling voltage (Direct piezoelectric effect). d,e) If a voltage of the same polarity or opposite polarity to that of poling voltage is enforced, the element will get longer or shorter, respectively.

Piezoelectric materials are crystalline ceramic materials and also manufacturing materials that have high piezoelectric coefficients, which requires post processing, which is called poling process. At the beginning, below the Curie temperatures each crystal has symmetry and has a dipole moment but no net overall polarization. Exposing material to large electric field gives an alignment that causes a net dipole to the element and net polarization. The dipoles are nearly aligned after poling process.

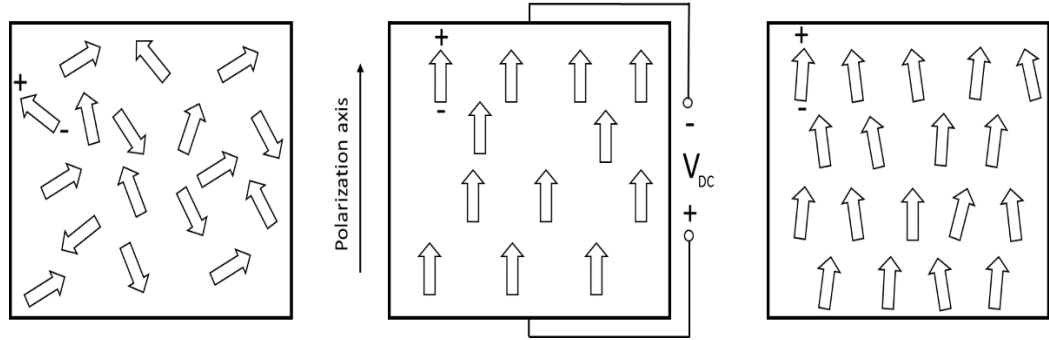


Figure 2. Poling process. Initially dipoles are oriented randomly. Applying large electric field force the domains to become oriented. After DC field is removed, remnant polarization is obtained.

1.1.2. Constitutive Equations

Properties of piezoelectric materials such as ceramics, polymers etc. are different in particular crystal plane directions. Electromechanical properties of piezoelectric materials standardized by IEEE Standards on piezoelectricity, which assumes a low electric field and mechanical effects piezoelectric materials show linear behavior [41]. Polarization direction and typical hysteresis curve and schematic of the material in order to characterize piezoelectric properties were given in Figure 3. Relation between polarization and applied electric field (Eqn. 1) which corresponds to switching response of the material is given by [42]:

$$P = D - \varepsilon E \quad (1)$$

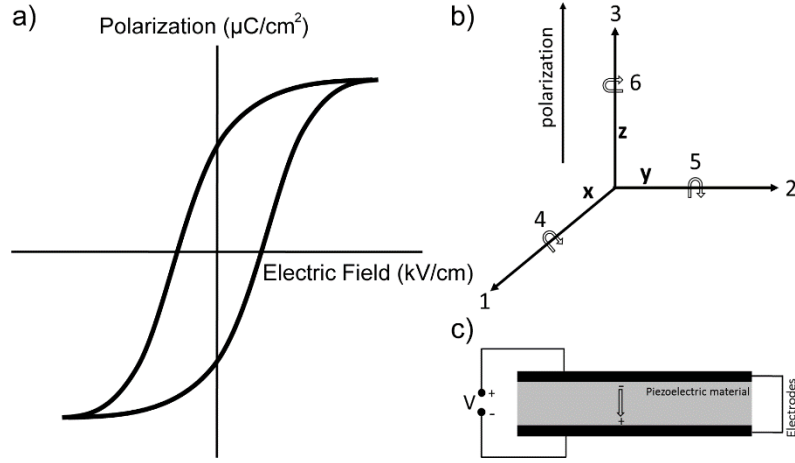


Figure 3. Polarizing directions and effects of electric field for polarizing mechanism. a) Typical curve of change in the polarization with electrical field. b,c) Direction of forces on a piezo element. Indirect or direct polarization can be characterized by polarization hysteresis.

Basic constitutive equations for linear piezoelectricity were established by IEEE Standards in 1987.

$$D_i = e_{ij}^\sigma E_j + d_{im}^d \sigma_m \quad (2)$$

$$\varepsilon_k = e_{jk}^c E_j + e_{sk}^E \sigma_m \quad (3)$$

This formulations can be written in matrix form:

$$\begin{bmatrix} D \\ \varepsilon \end{bmatrix} = \begin{bmatrix} e^\sigma & d^d \\ e^c & e^E \end{bmatrix} \begin{bmatrix} E \\ \sigma \end{bmatrix} \quad (4)$$

Piezoelectric coefficient d can be written in 3 dimensions,

$$d = \begin{bmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{32} \\ 0 & 0 & d_{33} \\ 0 & d_{24} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (5)$$

P . . . Polarization (C/m²)
 D . . . Electric Displacement (C/m²)
 ϵ . . . Dielectric permittivity (F/m)
 E . . . Applied electric field (V/m)
 ϵ . . . Strain vector (m/m)
 d . . . Piezoelectric coefficient (m/V or C/N)
 σ . . . Stress vector (N/m²)
 S . . . Elastic compliance (m²/N)

Applications of piezoelectricity generally depends on electromechanical considerations, which plays a major role in conversion of mechanical energy into electrical energy. They are used in various applications, such as pressure sensors, memories, microphones, sonars, energy converters etc. [43-45]. There are many more examples of piezoelectricity related applications, which carry great importance due to their use in mechanics and electronics. Figure 4 gives application summary of the piezoelectric technology by utilizing direct effect and converse effect.

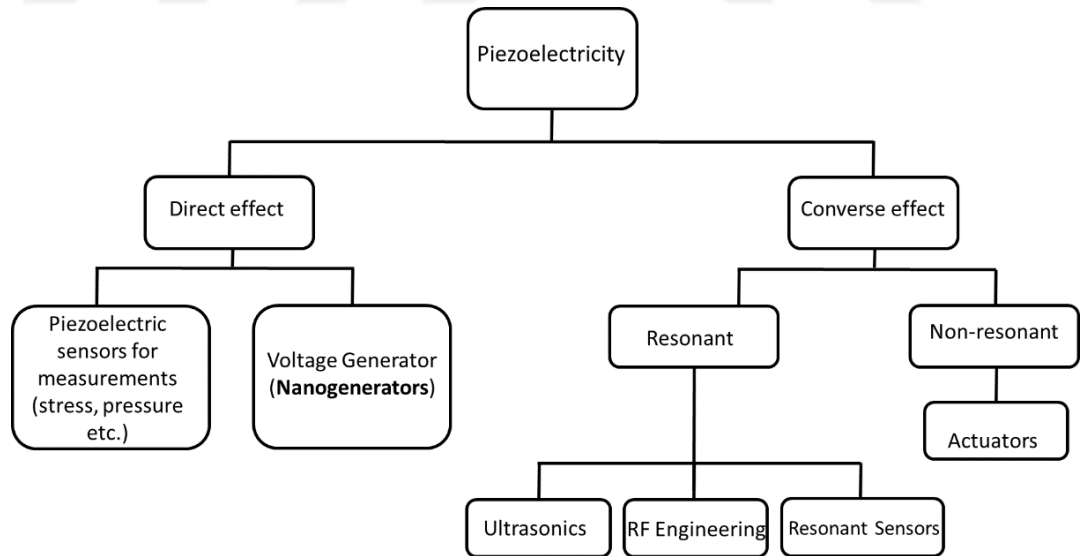


Figure 4. Applications of Piezoelectricity

In general, there are several drawbacks of piezoelectric materials, such as brittleness, toxicity, high cost production. Desired properties of piezoelectric materials are:

- Compatible with mass production (low cost and easy processing)
- High piezoelectric coefficients
- High mechanical resistance (high durability)
- Non-toxic components

Piezoelectric polymers are good candidates to fulfill these requirements and since the discovery of piezoelectric polymers, namely PVDF and its copolymer VDF-TrFE, they have been used in biology-related applications such as nanomedicine, tissue engineering and biocompatible implants and devices [46].

1.2. Carbon Nanotubes

Carbon nanotubes are rolled up version of 2D dimensional material graphene which was discovered by Iijima in 1991 [47]. Carbon nanotubes (CNT) are unique materials due to their mechanical and electrical properties. They are mechanically strong, 1D structures and they have remarkable charge transport properties, and they confine electrons to move along the length. There are two kinds of CNT: single wall carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) as shown in Figure 5. The SWCNT is a hollow cylinder based on carbon atoms with a diameter between 0.5 to 5 nm and the lengths are on the order of micrometers to centimeters. MWCNT has multiple nested cylindrical structures with the spacing of 0.34 nm. Diameters of MWCNT are ranging from 5 to 120 nm.

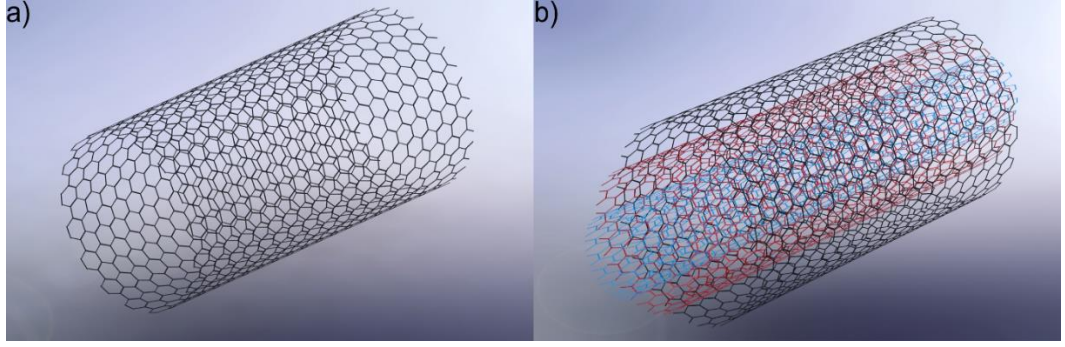


Figure 5. Representation of SWCNT (a) and MWCNT (b)

The structure of nanotubes is derived from the graphene sheet. The concept of a chirality is used to classify different types of CNTs. Figure 6 shows the honeycomb lattice of graphene and the lattice vectors of $\mathbf{a}_1$ and $\mathbf{a}_2$, defined on x-y plane [49]:

$$\mathbf{a}_1 = \left[\frac{\sqrt{3}a}{2}, \frac{a}{2} \right], \quad \mathbf{a}_2 = \left[\frac{\sqrt{3}a}{2}, -\frac{a}{2} \right]$$

where a is Bravais lattice constant, $a = 2.46 \text{ \AA}$. The structural characterization of CNT is defined by three parameters: the chiral vector $\mathbf{C}_h$, the translation vector $\mathbf{T}$ and the chiral angle θ . For different types of CNTs, equations regarding these parameters are given in the Table 1.

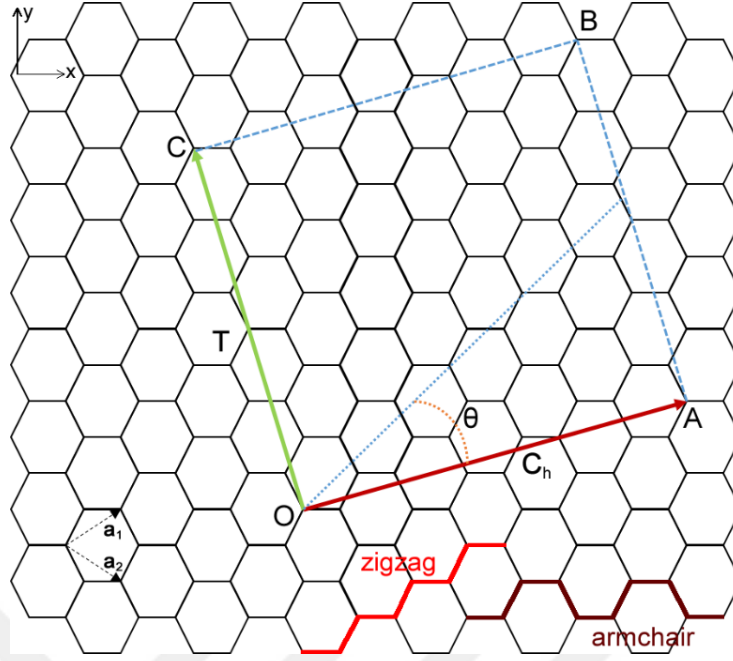


Figure 6. Illustration of conceptual construction of a honeycomb lattice. OCBA is a typical 1D unit cell for SWCNT. Zigzag and armchair structures in CNT lattice.

Symbol	Name	cCNT	aCNT	zCNT
$\mathbf{C}_h$	chiral Vector	$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 = (n, m)$	$\mathbf{C}_h = (n, n)$	$\mathbf{C}_h = (n, 0)$
C_h	length of chiral vector	$C_h = \mathbf{C}_h = a\sqrt{n^2 + nm + m^2}$	$C_h = a\sqrt{3}n$	$C_h = an$
d_t	diameter	$d_t = \frac{a}{\pi} \sqrt{n^2 + nm + m^2}$	$d_t = \frac{an}{\pi} \sqrt{3}$	$d_t = \frac{an}{\pi}$
θ	chiral angle	$\cos \theta = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}}$	$\theta = 30^\circ$	$\theta = 0^\circ$

Table 1. Table of structural parameters and equations for CNTs. cCNT stands for chiral CNT, aCNT armchair CNT, zCNT for zigzag CNT.

Chirality concept is important in order to understand type and the structure of CNT. There are three types of CNT, chiral CNTs, armchair CNTs and zigzag CNTs. These three types of geometries are illustrated in Figure 7.

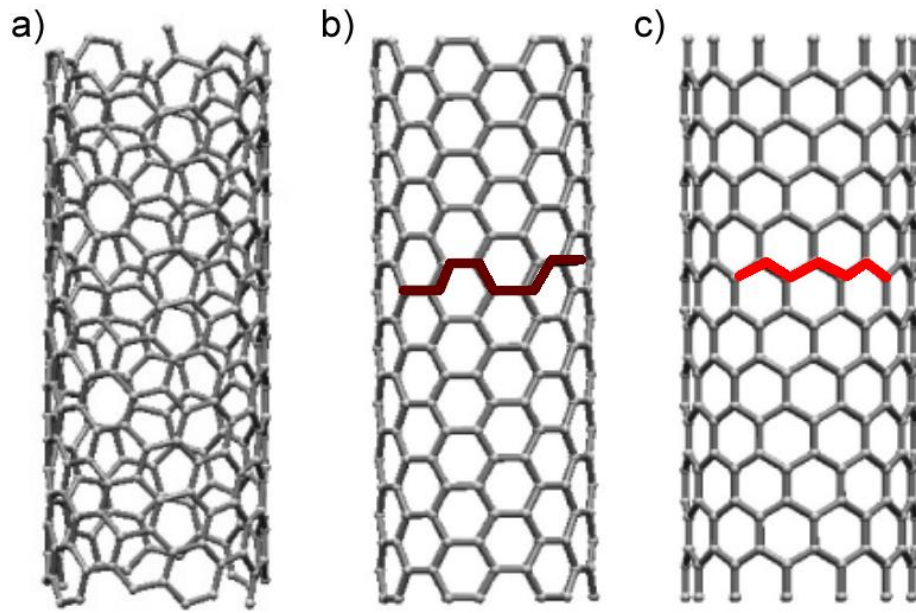


Figure 7. Adopted from [48]. Three types of SWCNT: a) chiral, b) armchair, c) zigzag CNT

The motion of electron in one dimensional structures such as nanowires, CNTs, nanotubes etc., is in the form of scattering and ballistic transport. Electronically, CNTs can be metallic or semiconducting, and this variety makes CNTs very attractive for many applications [50].

For ideal conditions, electron can be transported without any scattering, this is known as ballistic transport (Figure 8). CNTs can be considered as a 1D quantum wire, the motion of electron is in representation of a quantum conductance, quantum capacitance and kinetic inductance [48, 51].

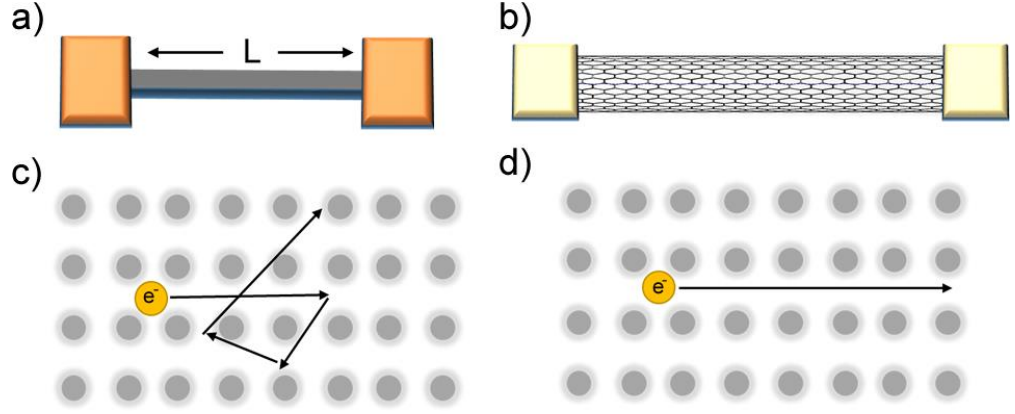


Figure 8. Schematic representation of two wire devices and types of electron transportation. A) A quantum wire between two contacts. b) SWCNT between two contacts. c) Illustration of electron scattering. d) Illustration of ballistic transport where an electron travels with a constant energy and momentum.

Electron scattering can be controlled by several parameters: by lowering the temperature, using very pure materials and smaller the conductor length in order to increase the possibility of the charge transport that is ballistic. Ballistic transport is a nanoscale phenomenon and quantum electrical properties starts with the understanding of quantum conductance/resistance.

The main expression for the ballistic current is:

$$I = \frac{2e^2}{h} N_{ch} V \quad (6)$$

Then, the quantum conductance G_q is,

$$G_q = \frac{dI}{dV} = \frac{2e^2}{h} N_{ch} = G_0 N_{ch} \quad (7)$$

where, N_{ch} if the total number of propagating modes or channels, h is the Planck's constant, e is the electron charge, G_0 is the unit of quantum conductance. $G_0 \approx 77.5 \mu S$ or $\frac{1}{G_0} \approx 12.9 k\Omega$.

Chapter 2

High Performance Piezoelectric Sensors and Devices

We demonstrated possible applications of high piezoelectric coefficient piezoelectric nanowires, such as pressure sensors, cardiac devices, e-skin and prosthetic hand. We built proof of concept artificial skin for large area sensing and pressure location. Cardiac devices were designed in order to sense blood pressure from the various body points that could inform us about health status of an individual. Next, a model hand with pressure sensors, which mimics a real human hand, and can detect small pressure changes and capable of doing human hand functions such as hand shaking, holding an object was demonstrated. In addition to all these applications, the discrimination of the collected charges from the triboelectricity is demonstrated by manipulating the crystal structure and phase transition of the piezoelectric microwires.

2.1. Introduction

Dielectric materials play a significant role in flexible electronics, which requires light weight, non-toxic chemical composition, high chemical resistance, high dielectric constant and good flexibility, as observed in some polymers, which are the key properties in the field [1, 52]. Designing organic piezoelectric materials introduces the opportunity of manufacturing flexible, wearable and stretchable self-powering devices, where there is a greater demand for developing high performance, piezoelectric materials. PVDF and its copolymer PVDF-TrFE seem to be the best candidates for polymer piezoelectricity [53, 54]. However, only the beta phase of these materials represents high piezoelectric coefficients from among their three different conformations (alpha, beta and gamma), because of all-trans stereo-chemical conformation. Although, the piezoelectric phase can only be obtained by poling with electric field and mechanical manipulation, recently developed electrical polarization independent processes are promising for fabricating such high piezoelectric coefficient materials [25, 55]. Improvement in the high piezoelectric coefficient polymers depends on dimensional factors as well as the fabrication method. Piezoelectric polymers in form of 1D structures were known to be presenting better performance in comparison with the 2D and 3D structures. Despite this, they are less efficient in terms of performance and electrical output, 2D and 3D forms of piezoelectric polymers are still ahead in the market, because of easy handling, large scale integration and inexpensive manufacturing processes [56, 30, 39]. The challenging part is the manufacturing of macroscopic devices perfectly integrated with metal electrodes, which can simply interact with piezoelectric components in 1D structures such as nanowires and nanotubes.

Human skin is the largest organ of the human body. The skin consists of mechanoreceptors that can receive tactile information from the surrounding environment. As demonstrated in Figure 9, epidermis of the mammal skin is hosting different types of pressure sensors, each of them operates with different frequencies [57, 58].

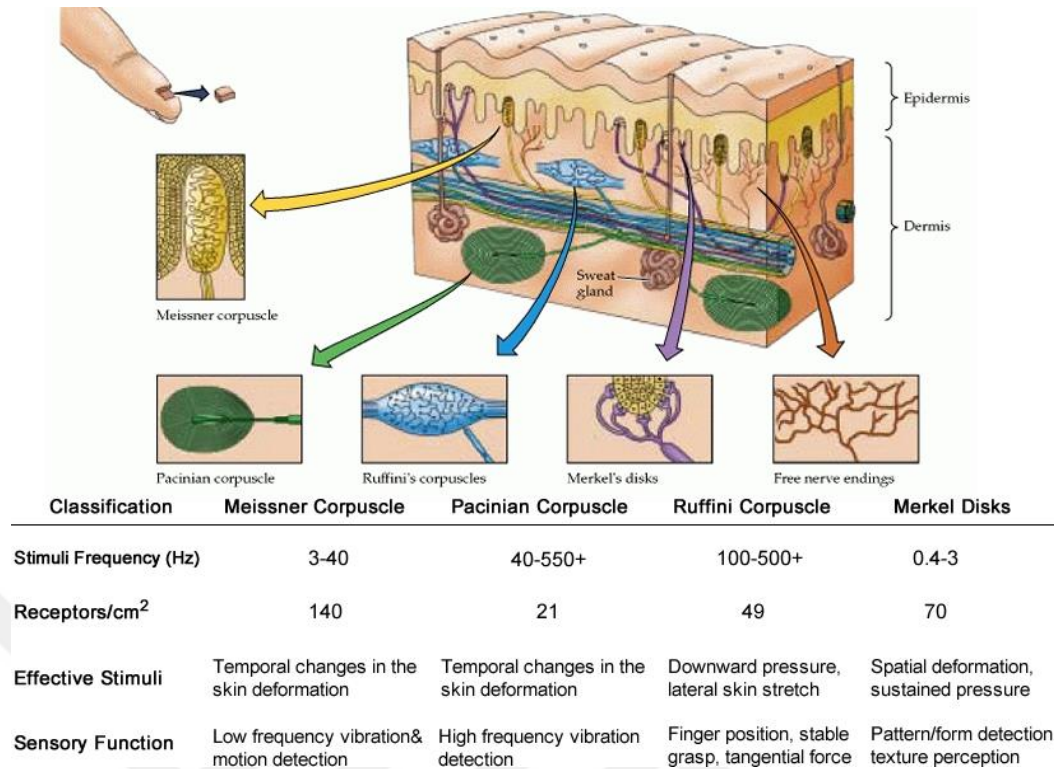


Figure 9. Schematic of human skin with various mechanoreceptors. Mechanoreceptors for receiving tactile information. Adopted from [57] and [58].

Large area, flexible, conformable and stretchable designs inspired by human skin are developed in order to sense pressure actuation and exhibit these signals in an electronic environment like the mechanoreceptors and neurons do. Electronic skins or artificial skins showed up to fulfill the aforementioned requirements. There are several types of transduction mechanism and methodological approaches to create e-skins [13]. In case of piezoresistivity transduction, characterization depends on change in the resistance or conductance of the sensitive material. Polymer composites filled with CNT, graphene and metal nanostructures have been proposed recently [59, 21, 60, 61]. Next, change in the capacitance would allow the researches to sense pressure depended capacitance in the sensitive material. CNT-based elastomers and PEDOT: PSS /PDMS structures were used to implement an artificial skin model [62, 63]. The ability to convert mechanical actuation to electrical signals makes the piezoelectric structures (thin films or micro and nanowires) best materials for the e-skin. PZT and ZnO are known as common piezoelectric material that can be implement with the conductive electrodes making the simplest configuration to design e-skins [64, 65]. Piezoelectric polymers such as PVDF and its copolymer PVDF-TrFE was used in several examples

of the artificial skins. In addition, transistor based e-skins have been proposed to be used as pressure sensitive rubbers in drain section of the transistor as a resistive material, which controls the current flow through the resistor, where the characterization depends on current mapping [16,66,14,19].

In recent years, flexible biomedical devices attracted lots of attention because they can give information about the health status of the patients or the individuals. Cardiac devices can count heart rates, measure blood pressure and collect heart rate signals from several body parts. Human skin requires ideal devices that are flexible, conformably mountable on the skin and operate without being decomposed or break down. Several devices can sense blood pressure of the animal or human, even respiration processes. These devices are mainly based on piezoelectric or piezoresistive materials such as PZT and PVDF-TrFE [61, 64, 36, 67]. In addition to pressure sensors that can inform human health status, prosthetic hands are very important to individuals' life quality. The efforts to create a prosthetic hand or model hands increases more rapidly that can sense pressures like the human hand is sensing mechanism. Examples of several model hands can be summarized as: Piezoresistive nanocomposite sensors were placed onto a glove that can sense finger movements [68, 69], and the sensors can be embedded into an industrial level prosthetic hand and that device can sense touch like the real human hand [70]. However, a model hand that is a close replica of the human hand that can sense touch, shear forces and pressure actuations from the environment still have not been proposed. The design considerations, materials and methods to achieve the prosthetic hand requirements and a prototype will be demonstrated in the upcoming sections. Several types of artificial skins, prosthetic hand and pressure sensors are shown in Figure 10.

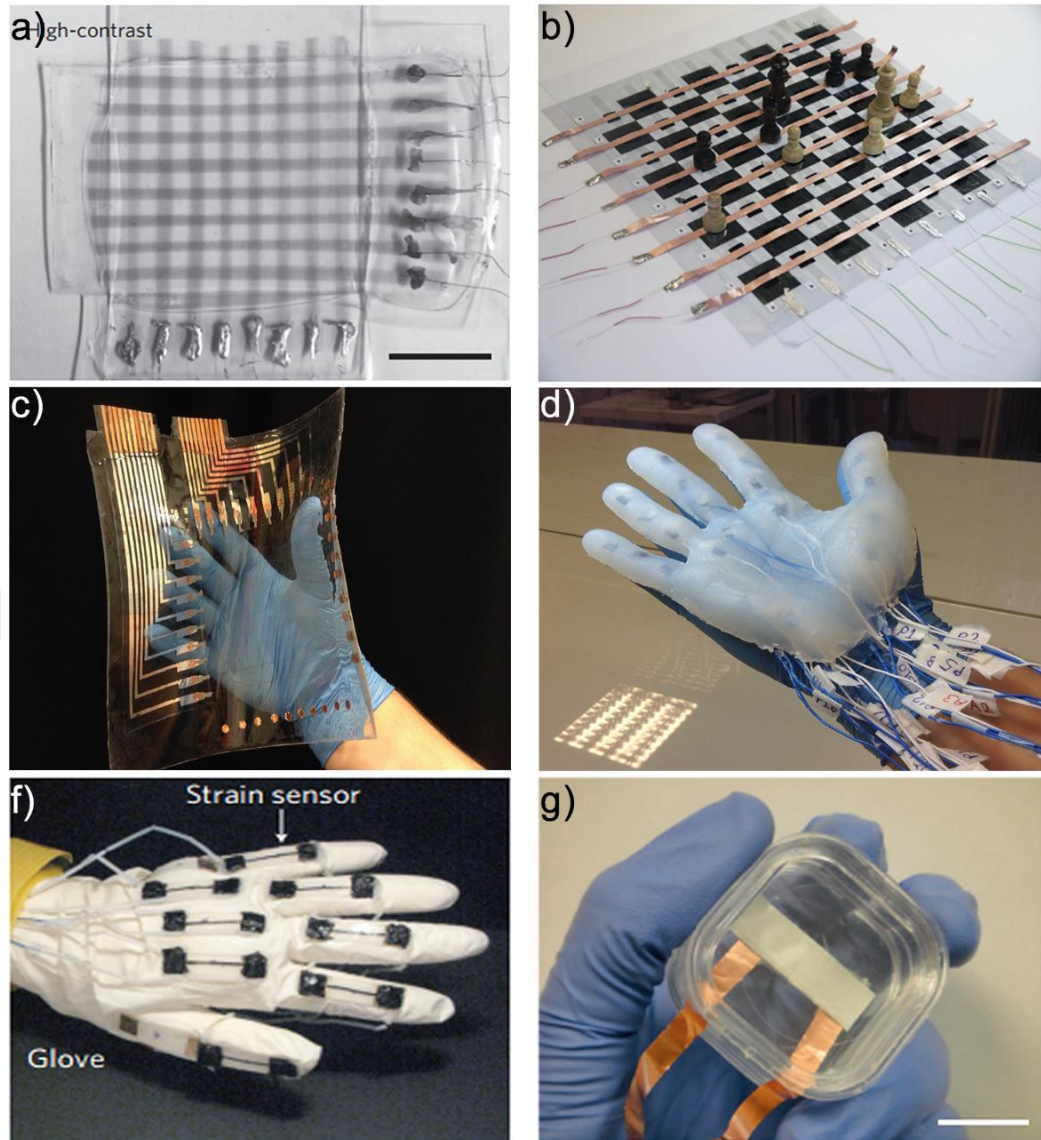


Figure 10. Examples of pressure sensitive electronic skins, model hands and sensors. a) [62], b) [59], f) [68], g) [53].

2.2. Nanostructured Piezoelectric Polymers

Owing to their unique properties (electrical, mechanical and thermal), one dimensional systems such as nanowires, rods, nanotubes are recently been investigated intensively [71]. Geometrical confinement at small scales around 100 nm has an influence on the properties of the materials. Piezoelectric polymers such as PVDF and PVDF-TrFE have different chain orientation and crystallization when geometrically confined. The most common piezoelectric polymer, PVDF has different phases; α , β ,

γ , δ , ϵ , among them, α is called the nonpolar and β is called piezoelectric (ferroelectric) β phase [25, 30, 18]. During the recent years, PVDF's copolymer PVDF-TrFE is commonly used in applications and deeply investigated due to its predominant β phase and high piezoelectric coefficients (d_{33} and d_{31}). In addition to its remarkable properties, PVDF-TrFE is flexible biocompatible, light weight and non-toxic. Several approaches are represented to confine PVDF-TrFE polymer into 1D structures for achieving high piezoelectricity and designing functional devices [30]. Typically, these 1D structures PVDF-TrFE structures can be synthesized using four main techniques: template assisted method with using a porous matrix or membrane [39, 72-77], nanoimprinting [55, 78-84], electrospinning [53, 85, 86], and thermal fiber drawing [23, 25].

Template assisted approach uses the infiltration of the polymer solution or polymer melt into the as-prepared porous matrix. Using this technique, nanowires and nanotubes, which are sub-100 nm in diameter can be fabricated. However, this technique suffers from low piezoelectric coefficients, large area fabrication and uniformity [72, 73]. Uniform arrays of piezoelectric nanopatterns can be obtained by the nanoimprinting method [78]. This lithography type uses the inverse replica of the patterns on the mask, where the mold is hot-pressed above the melting temperature of the polymer [83]. The maximum piezoelectric coefficient ever reported is 210.4 – pm/V, which is a nanograin structure with a dimension of 20 nm [55]. Electrospinning is another tool to obtain nanoscale polymers, where under the intense electric field polymer solvent solution is extruded from a nozzle [53, 87, 88]. Nevertheless, this fabrication technique lacks creation of aligned fibers and the diameters are mostly not below 300 nm. Finally, a recent novel fabrication technique is called thermal fiber drawing technique, this become a dominant technique to fabricate highly crystalline, high piezoelectric coefficient nanoribbons. The ability of the getting well-aligned, ordered, long and highly crystalline piezoelectric micro and nanowires would pose fabrication method that paves the way for functional, highly sensitive devices and sensors [25].

The piezoelectric properties and crystalline structure of the piezoelectric materials can be investigated by PFM (Piezoresponse Force Microscopy), XRD (X-Ray Diffraction) and FTIR (Fourier Transform Infrared) analysis. PFM is a scanning probe

technique that extracts piezoresponse hysteresis loops, which is created by the dipole orientation, while a certain voltage manipulates the domains of the crystal [80, 89]. From the PFM signal, the magnitude of the piezoelectric coefficient d_{33} can be calculated. The macromolecular orientation and crystalline structure of the material can be determined by wide angle X-Ray diffraction and FTIR spectroscopy. The peak assigned to the piezoelectric β phase is around $2\theta = 20^\circ$, which represents the (110) and (200) orientation. Intensity changes and its shifts from this value, determines the crystallinity of the polymer. FTIR spectrometry is a verification of XRD analysis; corresponding β peaks can be determined in order to analyze the phase of the material [90, 91]. A broad explanation of the data analysis of the XRD and FTIR characterization will be given in chapter 3.

Study	d33 (- pm/V)	Fabrication Method	Geometry	Phase
[39]	10-20	Template - Assisted	Nanowires (5-10 nm)	β
[72]	6.5-8	Template - Assisted	Nanowires (50 nm)	β
[73]	-	Template - Assisted	Lamellas (30 nm)	-
[74]	25-45	Template - Assisted	Nanowires (40 nm)	β
[75]	-	Template - Assisted	Nanotubes (250)	β
[76]	-	Template - Assisted	Nanotubes (200 nm)	-
[77]	-	Template-Assisted	Nanorod (120 nm)	β
[78]	-	Nanoimprinting	Nanocells (50 nm)	β
[79]	-	Nanoimprinting	Hexagonal (400 nm)	-
[55]	210.4	Nanoimprinting	Nanograss (Sub 20 nm)	β
[80]	48 - 81	Nanoimprinting	Nanopatterns (200 nm)	β
[81]	-	Nanoimprinting	Nanodots (80 nm)	β
[82]	-	Nanoimprinting	Nanocells (250 nm)	β
[83]	-	Nanoimprinting	Nanodots (40 nm)	β
[84]	-	Nanoimprinting	Nanopattern (300 nm)	β
[85]	-	Electrospinning	Nanofibers(500 nm)	β
[53]	-	Electrospinning	Nanofiber (260 nm)	β
[86]	-	Electrospinning	Nanofiber (700 nm)	β
[25]	58.5	Thermal Drawing	Nanowire (5 nm)	γ (PVDF)
This Study	320	Thermal Drawing	Nanowire (400 nm)	β

Table 2. Piezoelectric Properties of Nanostructured PVDF-TrFE Polymers Reported in the Literature.

Figure 11 demonstrates the PVDF-TrFE micro and nanoribbons that are produced as a results of first and second step iterative fiber drawing processes. We etched and extracted the piezoelectric fibers out of the PES cladding in a length of 15 cm for large area applications (Fig.11-D). Images of etching and extraction of the fibers are given in the figure 12.

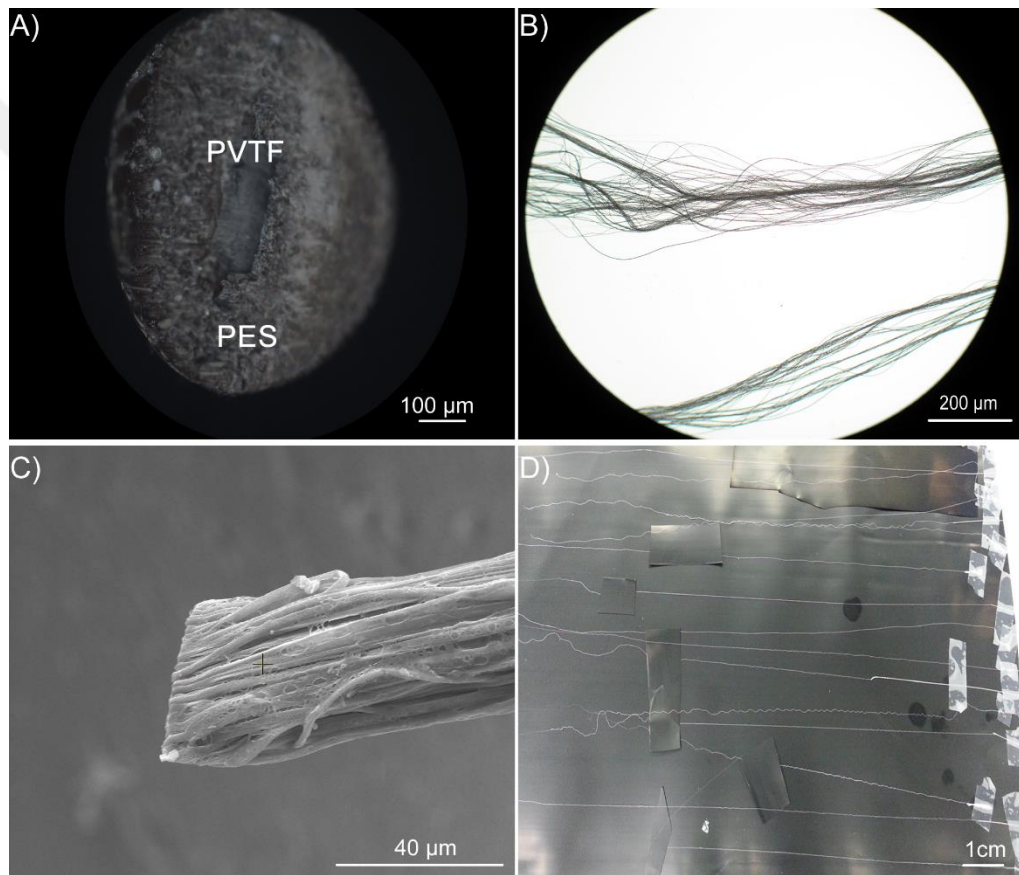


Figure 11. Optical and SEM images of 1st step and 2nd step PVDF-TrFE Fibers. A) Cross sectional image of the first step PVTF microfiber in the PES cladding. B) Photograph of etched P (VDF-TrFE) nanoribbons. C) SEM image of second step nanoribbons. D) Optical image of etched fibers for large area applications.

Each of the individual fiber is 400 nm in width and a bundle of PVDF-TrFE fiber consists of approximately 400 hundred nanofibers, which takes shape of a flexible, long bundles and represents high piezoelectricity.

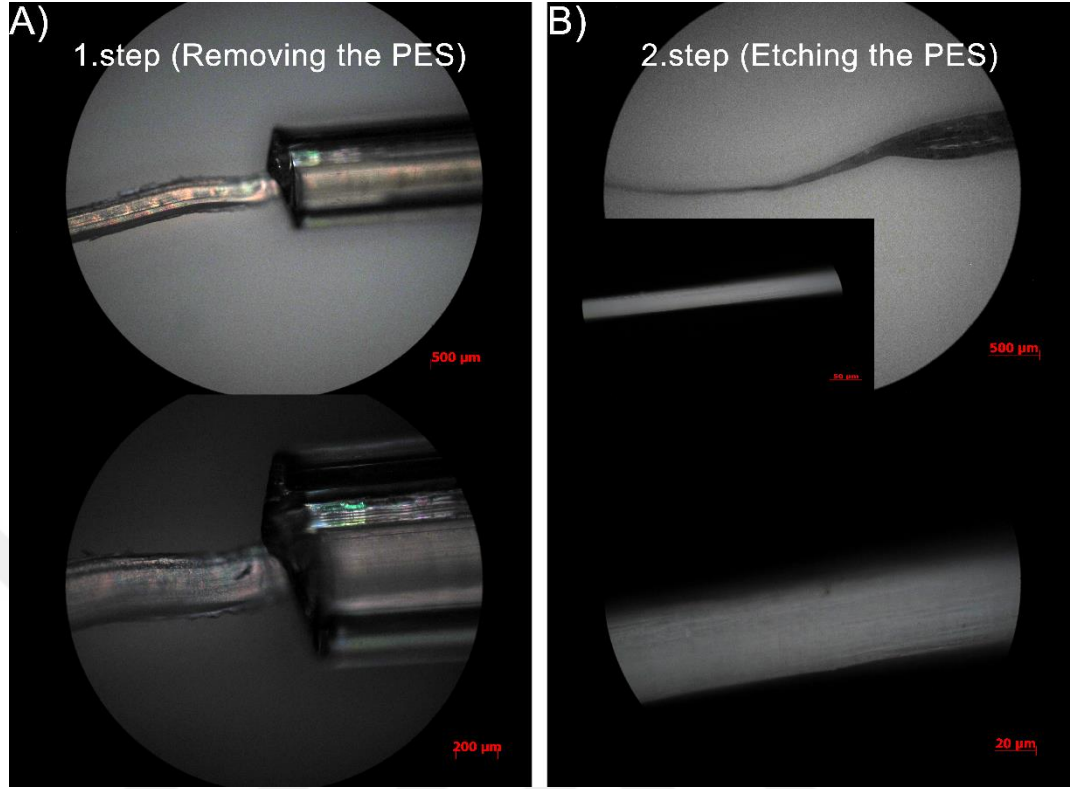


Figure 12. Optical images of 1st step extracted piezoelectric fibers and 2nd step etched nanoribbons. A) First step PVDF-TrFE fibers extracted out from the PES cladding. B) Optical image of etched second step nanoribbons, Inset shows the fine fiber surface.

2.3. Large Area Artificial Skin

For designing large area applications we used second step 15 cm long PVTF fibers which are dense, flexible and lightweight. One of the important application of using piezoelectricity is a device that can sense pressure changes like our skin, is an electronic skin [53, 62]. In this section, we designed and characterized large area, transparent and flexible 10 by 10 artificial skin matrix.

2.3.1. Fabrication

Fabrication step is started with preparing PDMS layer, which provides device with flexibility and holds all components together. In the preparation of PDMS, base and curing agent are mixed in 10:1 ratio. The mixture is degassed for 1 hour under 10^{-2} Torr vacuum pressure, after pouring PDMS onto PMMA substrate, structure is held at

room temperature for 2 days. Next, 20 PVTF fibers are etched out from claddings in lengths of 15 cm, which are etched by DCM solution. Subsequently, only a single surface of the nanoribbons are coated with 100 nm thick gold by using e-beam evaporator (VAKSIS MIDAS PVD). Electrode design starts with mask preparation that is a classical, simple method for fabricating large area devices. Acetate is used as mask material, electrode structures and lines are drawn by Epilog laser cutting system and masks are placed onto Polyester (PET) film, then 1 μm is Aluminum deposited by thermal evaporator (VAKSIS Elif). Afterwards, Al is deposited PET films are cut in desired lengths and first electrode layer is placed onto PDMS layer along the vertical dimensions. Gold coated fibers are placed on each Al electrode and they are stacked using silver paste and circular copper tapes. 10 fibers are placed the same way with first part of the device encapsulated with 1 mm thick PDMS (Figure 13).

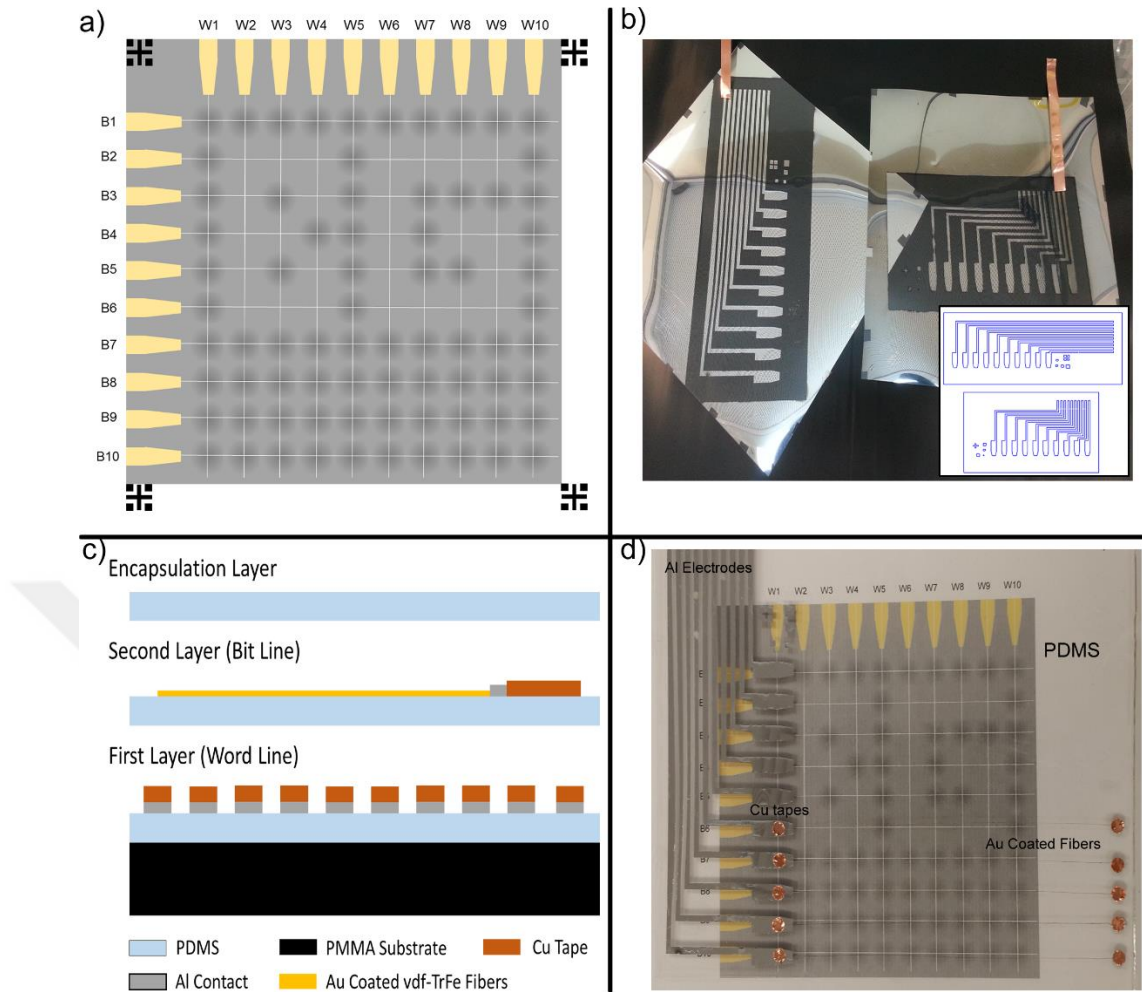


Figure 13. Fabrication steps for the artificial skin using second step fibers. a) Schematic representation of electrodes for large area e-skin device, word (W1-W10) and bit (B1-B10) lines are shown. b) Images of polymer masks for aluminum electrode fabrication, inset show the electrode schematic. c) Schematic illustration of artificial skin, materials and structures are shown. d) First layer of artificial skin with gold coated piezoelectric fibers, copper tapes and PDMS layer.

The second layer of the device was fabricated as it was done in the first step. Al coated PET electrode layer was placed onto PDMS layer, fibers were connected on the conductive parts and the entire device was then encapsulated with PDMS layer. Finally, the device is peeled away from the sacrificial PMMA substrate (Figure 14).



Figure 14. Optical image of fabricated large area electronic skin. Optical images of first and second layer images of electronic skin with letter 'B'. Bottom images demonstrate completed map transparency and flexibility.

The final structure of the device is flexible, capable of being rolled, transparent and can sense pressure changes from 20 cross-sectional points, which collect piezo-charges from both lateral and vertical nanoribbons.

2.3.2. Characterization

Depending on whether PVTF dipoles are in perpendicular orientation to the fiber axis when a mass is pressed or removed from the system, a positive or negative piezoelectric potential is produced and collected from the copper tapes, respectively. Figure 15a contains the equipment of the experimental setup. Voltage values were collected by TDS1012B two channel oscilloscope (Tektronix). Two oscilloscope probes were connected to corresponding sensor parts and when a force is applied in

cross-sectional direction to fiber sensors, the data were collected from two oscilloscope probes. To demonstrate pressure sensing mechanism of electronic skin, metal marble was placed on W8 and B8 lines, corresponding electrodes are connected to the two probes. Releasing the marble produced maximum 200 mV open circuit voltage, intensity map and generated voltage peak data is given in Figure 15.

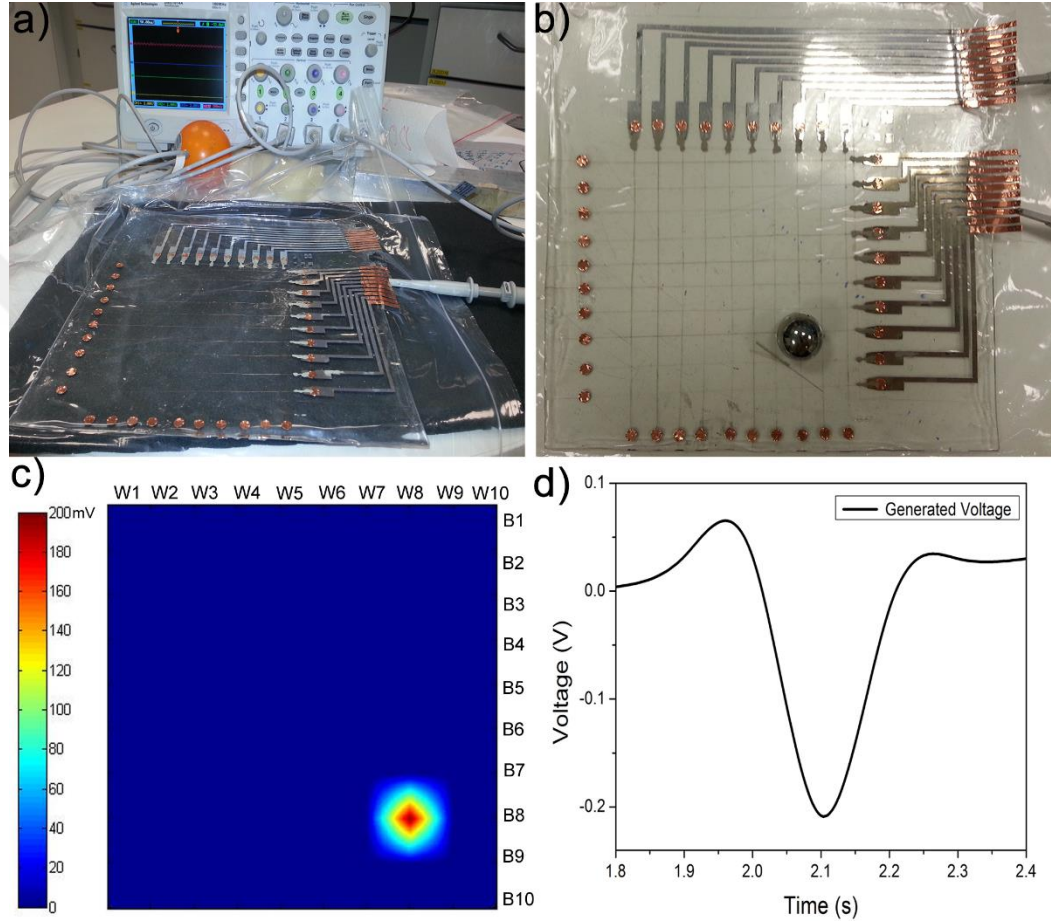


Figure 15. Electrical characterization of electronic skin. a) Optical image of experimental setup for the characterization of the piezoelectric device. b) Optical image of artificial skin with metal marble on W8 x B8 lines. c) 2D voltage signal intensity distribution measured from the 10 x10 e- skin matrix. Voltage mapping of the pressure distribution on W8xB8. d) Maximum open circuit voltage generated from the pressure that is applied by the marble.

In Figure 16, small pressure characterization was demonstrated. The aim of this characterization was to determine minimum pressure value that excites the piezoelectric fibers. Small values of masses (1-9 Pa) were dropped from the certain height (1-3) and the pressure was applied onto the single fiber, immediately charge is collected from the e-skin. Linear relationship between pressure and the output voltage

was demonstrated. Experimental data and fit were associated linearly. Inset shows the press and release peak of the charge collected from a single nanoribbon in the artificial skin.

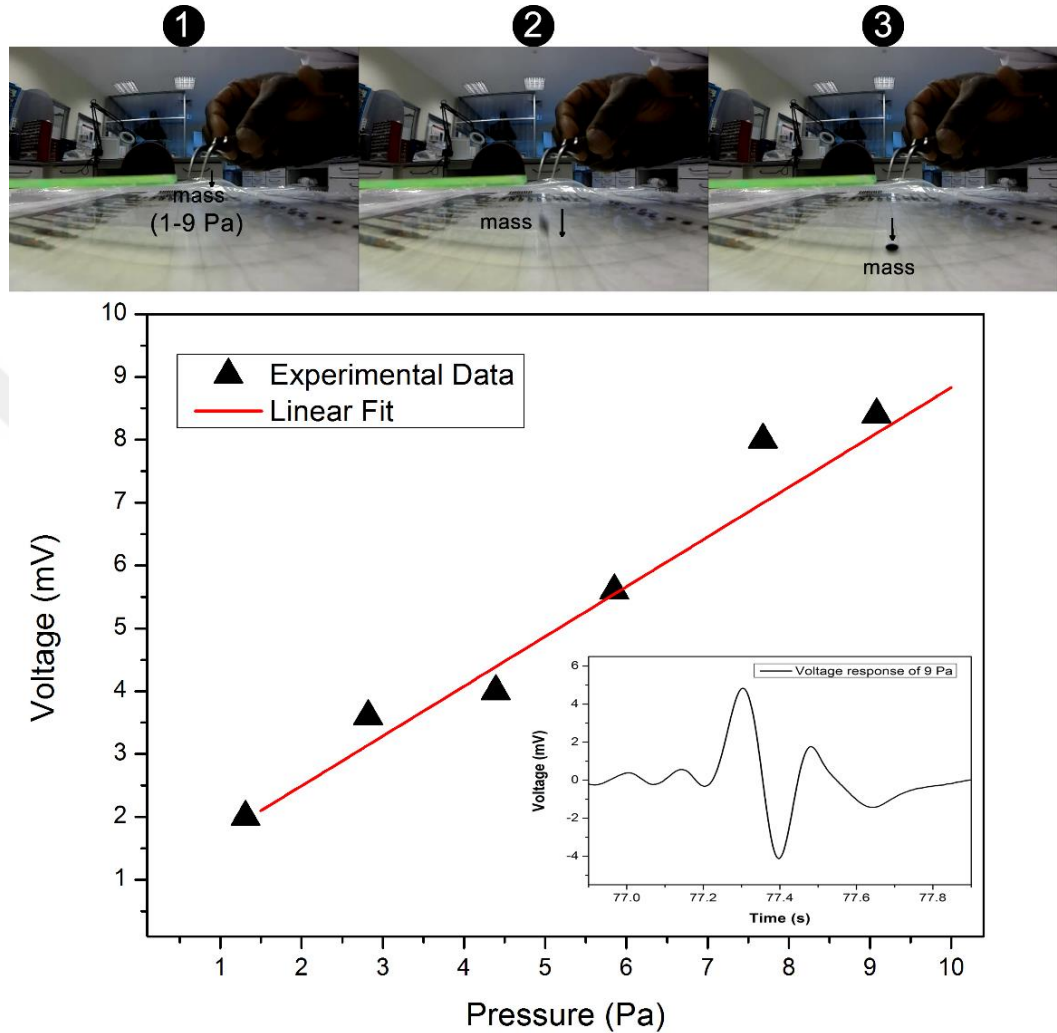


Figure 16. Small pressure analysis of single pixel element of e-skin. Experimental setup for the small polymer drops on to the artificial skin surface. Images (1-3) show the polymer mass falling from the certain height. Data shows the maximum generated voltage by increasing pressure values. Inset shows the voltage peak for 9 Pa pressure value.

2.4. Cardiac Sensor

Cutaneous pressure monitoring is a popular application for piezoelectric systems that can provide information about individuals' health status by measuring blood pressure and heart rate from body parts, for example, chest, arm and neck [64]. These

are devices which are mostly flexible and because they can conformably suit on the body parts, these pressure and temperature sensors are very convenient for wearable electronics.

2.4.1. Fabrication

The idea of hearth rate monitoring and sensing heart pulses with piezoelectric materials come to part with the rise of the flexible and stretchable electronics.

Cross-sectional schematic illustration of cardiac device and its components were demonstrated in Figure 17a. The fabrication process starts with preparation of 1 cm diameter circular PET substrate. Next, 100 nm Au coated piezoelectric fiber was placed onto the substrate, then contact material copper tape was connected to the fiber. Finally, whole structure was closed with PDMS and was encapsulated with flexible silicone.

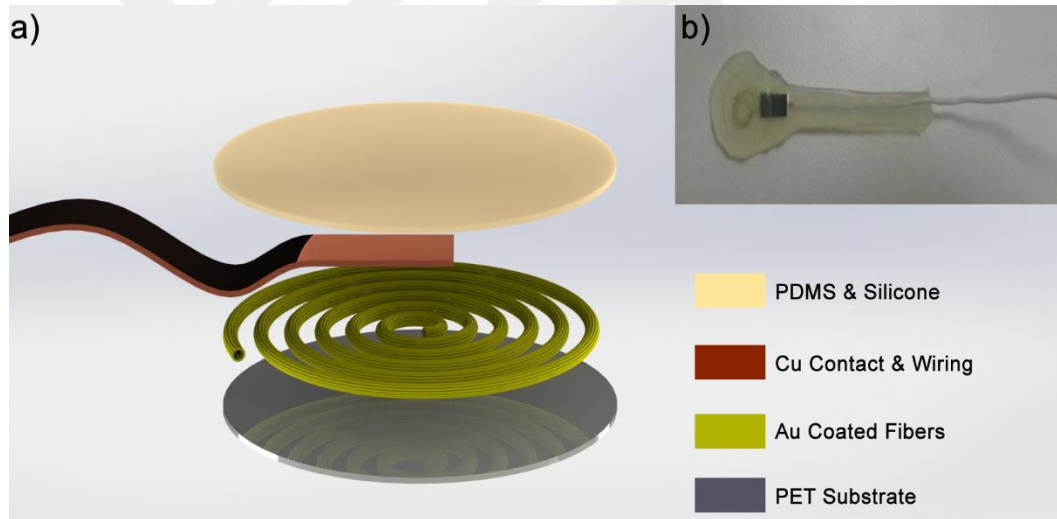


Figure 17. Schematic representation of cardiac sensors. a) Schematic of layers and device construction of piezoelectric nanowire electronic skin. b) Optical image of the designed cardiac device.

2.4.2. Characterization

Nanoribbon structure enables us to have high surface area and small confined structures in a single fiber; this results in a high piezoelectric constants. These properties enable the fiber-based structures to sense small pressure values, even blood

pressure from the skin. To demonstrate device capabilities, nanofiber-based cardiac device was mounted on the various points of the skin. Measurements from the wrist, arm and neck were given and corresponding photographs for each measurements were illustrated in Figure 18.

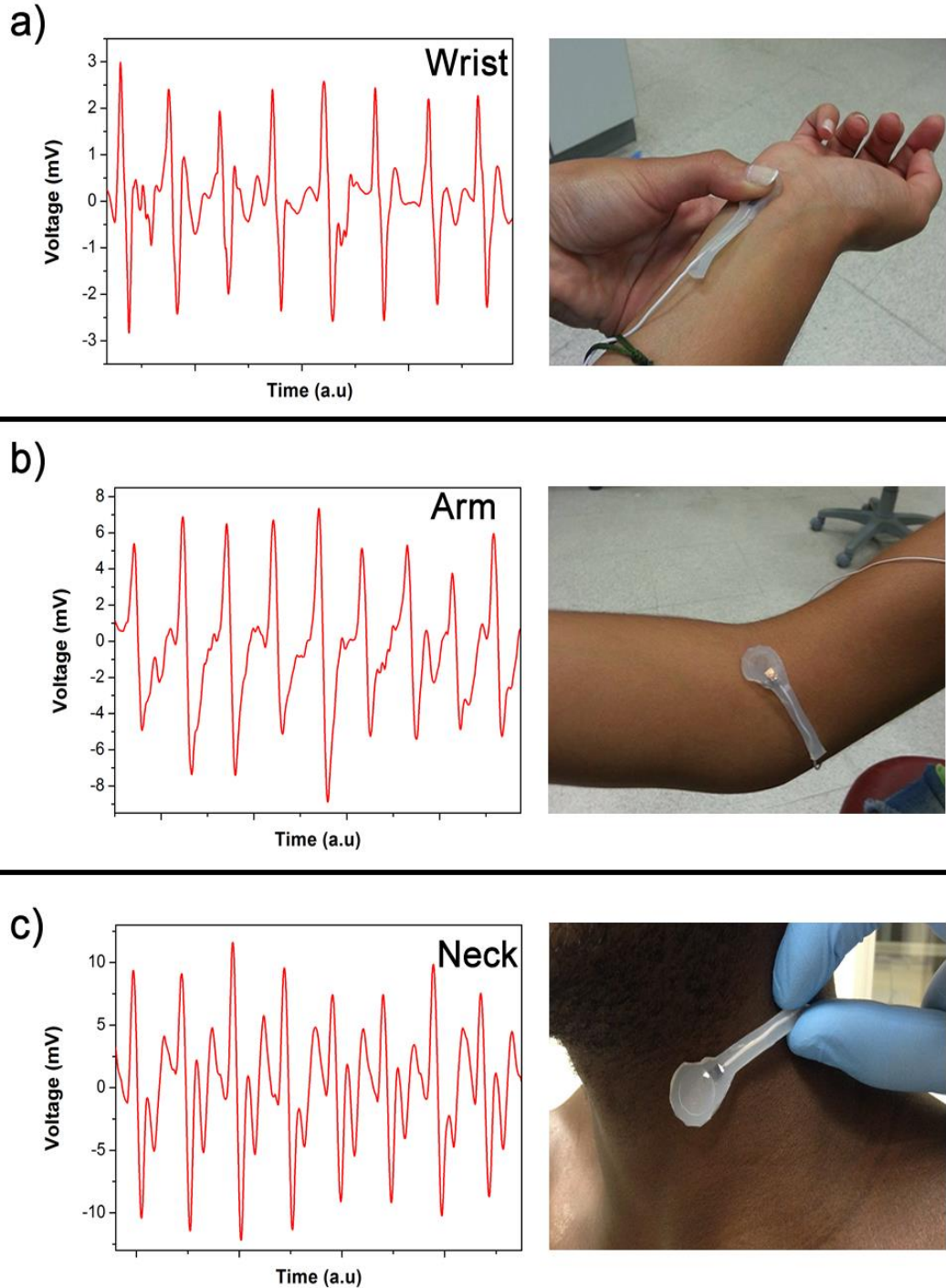


Figure 18. Blood pressure measurements on the wrist, arm and neck. a) Open circuit voltage (V_{oc}) - time plot for a sensor placed on the wrist and photograph of the sensor on the wrist. b)

V_{OC} - time plot for a sensor placed on the arm and photograph of the sensor on arm. c) V_{OC} - time plot for a sensor placed on the neck and photograph of the sensor on the wrist.

Open circuit voltage responses from the body parts can inform us about heart rate and heart rhythm. Demonstrations involved a healthy female and male in their twenties, no allergic reactions or damage to their skin were observed in our demonstrations. These applications demonstrates that highly sensitive nanofibers can be used in combination to medical electronics and wearable devices.

2.5. Model Hand with Pressure Sensors

Human skin contains cutaneous sensors, in other words mechanoreceptors that can convert mechanical stimulations to the electrical signals. A model hand for demonstrating this capability depicts how pressure sensors could be used in or to form a corporation into a prosthetic device [70]. Prosthetic arms and limbs are very crucial in the lives' of disables. The technology evolves to a high-tech, functional and sensory systems that is capable of collecting information from the surrounding environment. Here, we design hand-like device that senses pressure, fingertip touch and it could be placed over commercial prosthetic hands. Our device has 22 pressure sensors, which were placed into model hand that are embedded into flexible silicone material. The final view is a replica of a real human hand.

2.5.1. Fabrication

Fabrication of model hand starts with mold preparation from plaster blend that keeps all components of the device together in one piece. Primarily, plaster blend was prepared as a gel form, 1 kg plaster powder was mixed with 2 liters of water, and then the mixture was poured into a pot. A model limb, in this case human hand was pressed into the mixture and was kept till the mixture was got hardened (Figure 19b). The desired model to the plaster can be given by varying the input pressure and holding time. After the plaster has dried up and hardened, thin layer of silicone was poured into the mold that gives the structural layer in order to place pressure sensors. 22 pressure sensors were placed on the main sensing points of the hand. Connections were

checked for each sensor and they were stacked on the thin layer of silicone (Figure 19).

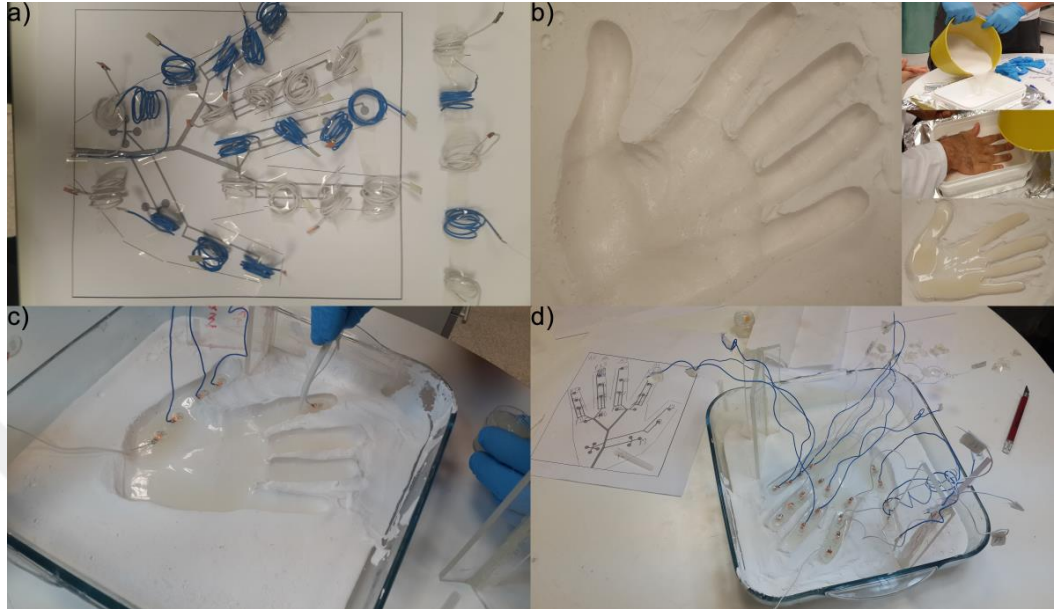


Figure 19. Fabrication steps for the model hand with embedded pressure sensors. a) Optical image of 22 pressure sensors prepared for embedding into the mold. b) Plaster mold preparation, inset optical images show mold and silicone hand design. c) First silicone is poured out into the plaster mold and after sensors are placed onto the dried silicone layer. d) Embedded 22 piezoelectric sensors into the plaster mold with silicone.

General schematic that illustrates pressure sensors in the model hand is given in Figure 20. The main material that can sense pressure changes is PVDF-TrFE piezoelectric polymer fibers which were developed in our group. The structural stiffness for fiber holding was provided by commercial polymer PET. For simplicity of placing sensors in finger positions, two different diameter sizes of PET platform were used for placing the sensors properly in the mold structure. 100 nm gold coated fibers were winded spirally on the PET polymer. Copper tape and long Cu wires were connected to the conductive parts of fibers and these processes were performed for each sensor. Finally the whole structure was encapsulated with silicone.

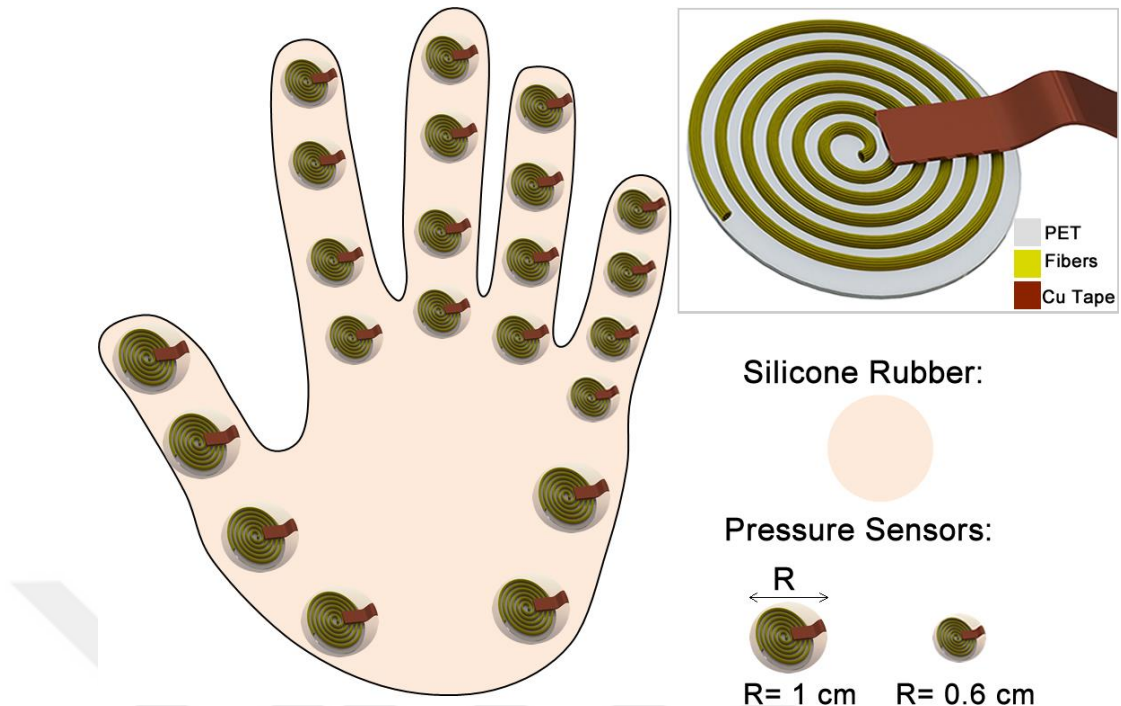


Figure 20. Schematic representation of model hand. Pressure sensors with different diameters embedded into silicone rubber, inset shows the layers of each pressure sensor.

Final structure and photographs of the model hand are given in Figure 21. Sensors and contact wires can be easily seen from the images when the hand is held from the palm. Whole structure is flexible and can employ human hand functions such as gripping, holding and hand shaking (Figure 21 right).

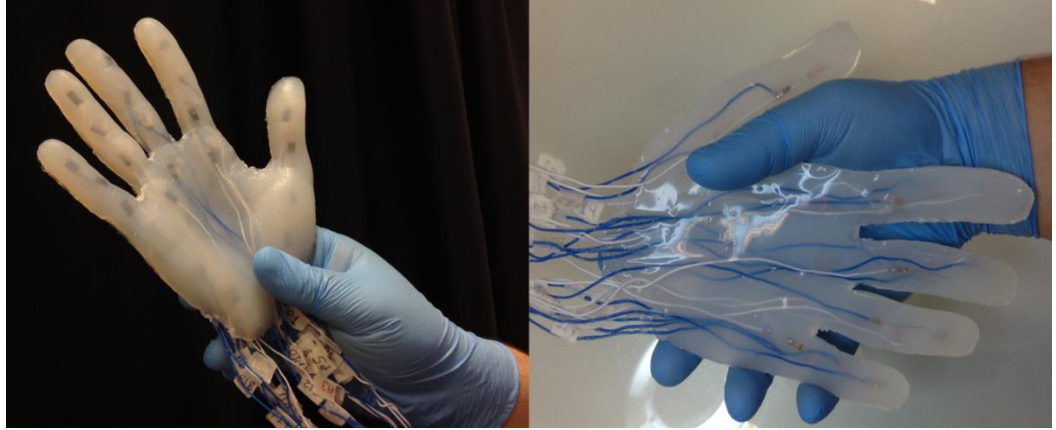


Figure 21. Optical images of model hand with sensors and wires. Photographs of labeled piezoelectric nanowire sensors with copper contacts embedded into silicone mold, the final structure is a model hand that can sense pressure values from various points.

2.5.2. Characterization

Model hand characterization leans on measuring open circuit voltage of each individual piezoelectric sensors. Each pressure sensor was labeled as P1-P22. Experimental setup consists of metal block that gives a certain pressure, PMMA that distributes the force and soft foam used as a support layer. In the setup, the model hand was placed on the soft foam and PMMA was laid on. Continuous pressure was applied to the system from 3 kg metal block (Figure 22 a-b). Measurements were performed by collecting charges from the four oscilloscope probes that were connected to four individual sensors while metal block was released from the experiment system. Release open circuit voltage values are given for each labeled sensors in Figure 22 c-f. The characterization was performed with the DS1014A four channel oscilloscope (Agilent Technologies), which enables us to check any crosstalk between the sensors. The variation in the voltage values (60 V- 100 V) can depend on the pressure distribution for each sensor. Besides, the model hand has different parts that were scaled in different heights, thus varying pressure distribution was unavoidable.

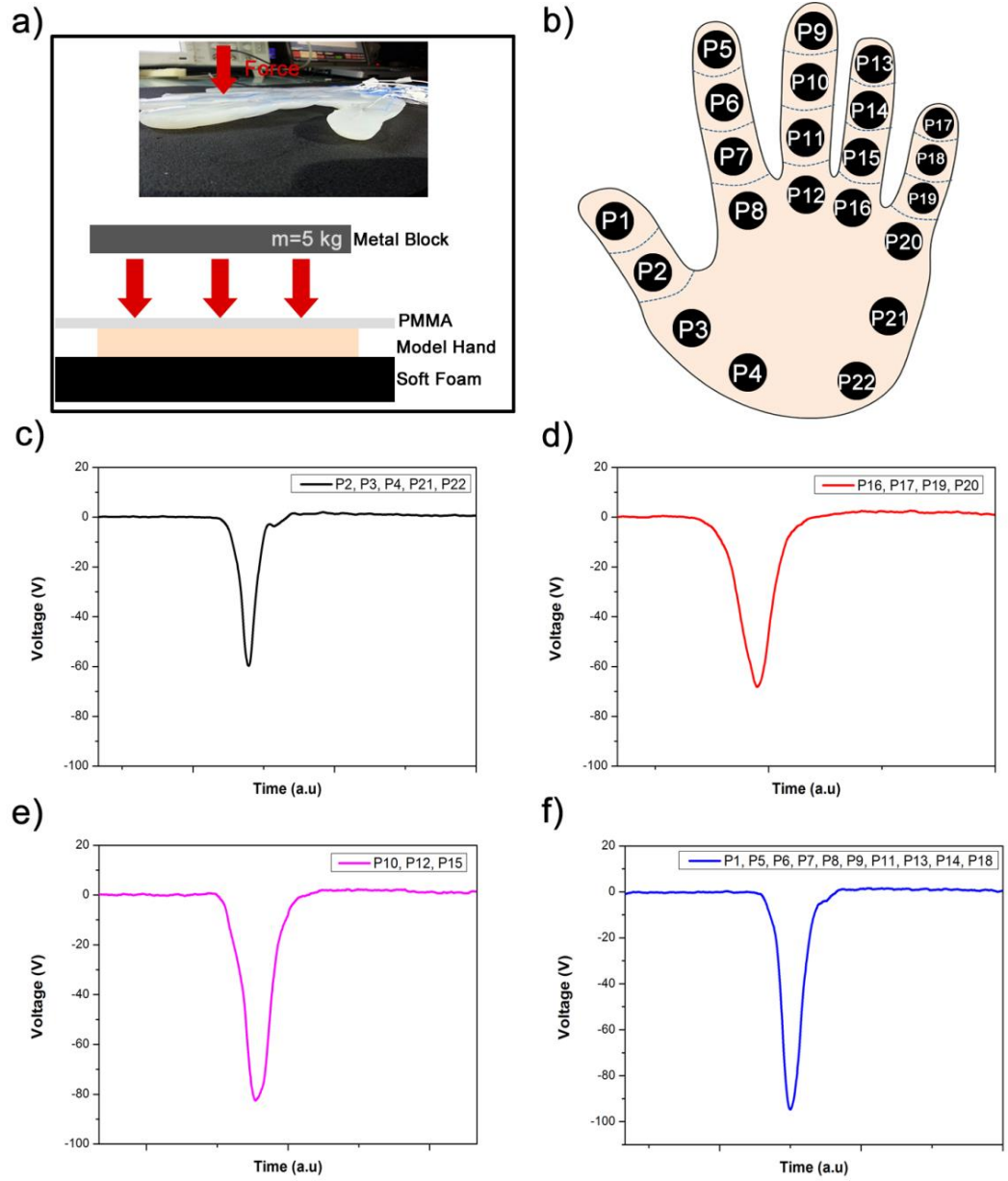


Figure 22. Electrical characterization of each pressure sensor in the model hand. a) Schematic representation for pressure actuation. b) Schematic representation of the labeled 22 pressure sensors. c-f) V_{OC} release peaks of the sensors at full contact position.

Mapping the intensity distribution is the best way to demonstrate characterization of multiple sensory systems. In order to illustrate each sensor's capacity, we present a 2D color voltage map for the model hand that gives an idea for performance of the device (Figure 23). Intensity distribution clearly presents the variation of voltage output values from the sensors. Hereby, outputs demonstrating any hand function will give an idea about the object that was manipulated by the hand.

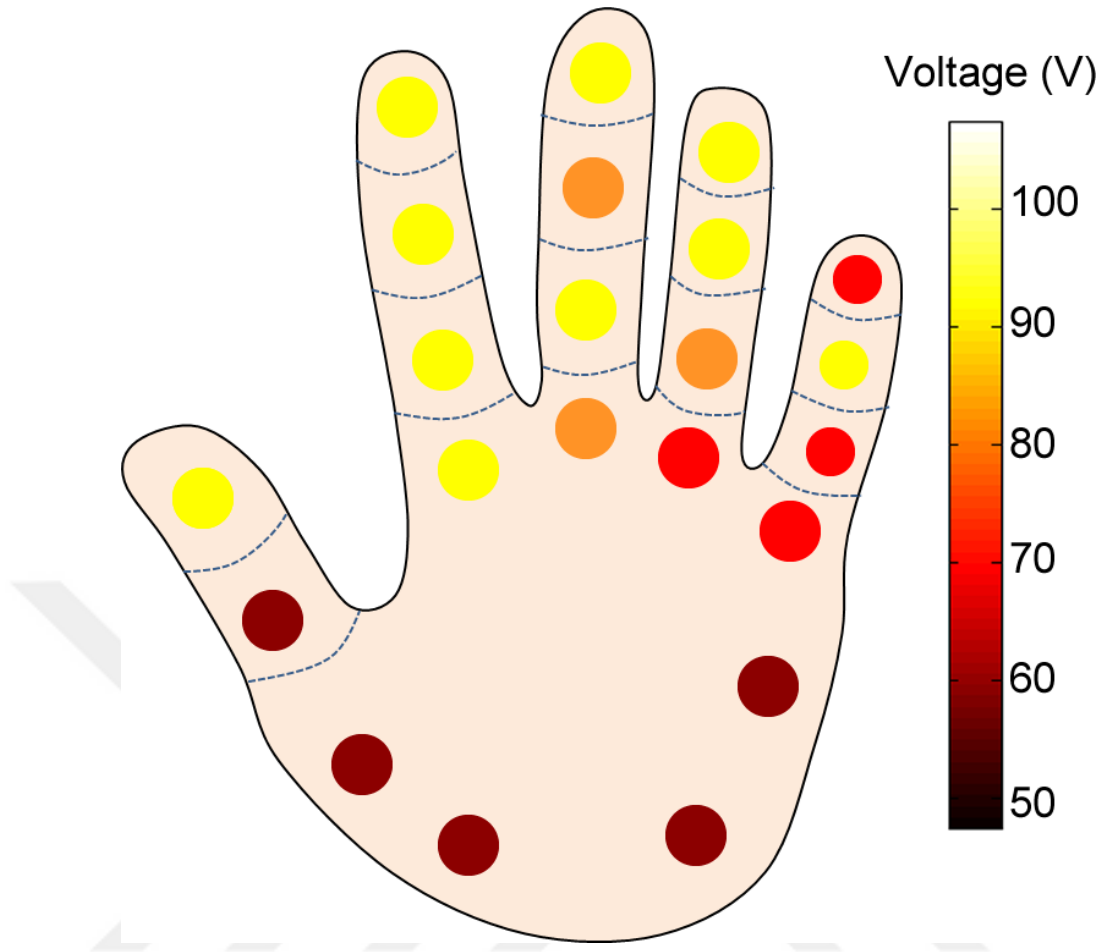


Figure 23. Mapping of a model hand for each pressure sensors. Open circuit voltage responses are ranging from 50 – 100 V for piezoelectric sensors. Voltage mapping of pressure distributions for the mass.

2.6. Controlling the Piezoelectricity

In order to deeply understand piezoelectric effect in our fibers, we performed several experiments for phase transition between nonpolar alpha phase and ferroelectric beta phase. PVDF-TrFE is a well-known piezoelectric polymer that is mostly in powder form and was found in alpha phase. However, beta phase is known as piezoelectric phase and most of its applications are demonstrated by using polymer material [30, 53]. Figure 24 represents the molecular structure of PVDF-TrFE. It is the copolymer of PVDF ($C_2H_2F_2$) and holds TrFE ($C_2H_2F_3$) chain. Figure 24b-c demonstrates the nonpolar alpha phase and piezoelectric beta phases of PVDF-TrFE molecular orientation. In alpha phase case, which is the phase where the material has the lowest piezoelectric coefficient, chains and molecules are not properly oriented

due to improper orientation of dipoles, thus the overall charge collected from the polymer is the low. On the contrary, for beta phase, molecules are oriented in a systematic manner, dipoles are oriented perfectly, and therefore highest piezoelectricity can be achieved in this form of polymer.

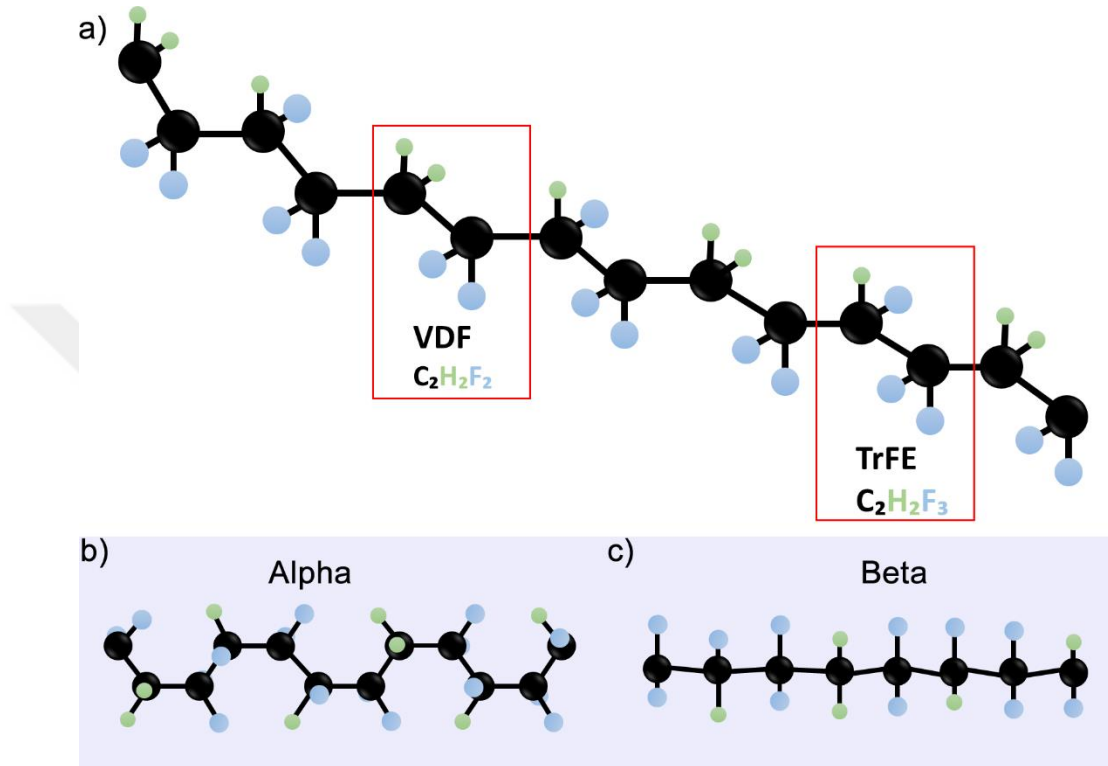


Figure 24. Molecular structure and phases of PVDF-TrFE. a) Molecular structure of the polymer that contains VDF and TrFE parts. b) Alpha phase demonstration of PVDF-TrFE. c) Beta phase demonstration of PVDF-TrFE.

As a first step for analyzing crystal structure of material, we performed XRD analysis of first step fibers that are annealed at both Curie temperature ($120^{\circ}C$) and melting temperature ($145^{\circ}C$) [92, 93]. Figure 25 demonstrates the XRD results of the fibers. $145^{\circ}C$ applied and as-drawn fibers demonstrates perfect beta phase that is clearly understand from the $2\theta \sim 19.9$, which corresponds the piezoelectric beta phase. In case of $145^{\circ}C$ annealed fibers, 2θ shifts to 20.2 that means crystals are not well oriented compared to the other fiber, less crystalline material [90]. The crystallinity of as-drawn fiber is between $145^{\circ}C$ and $120^{\circ}C$ annealed fibers that paves the way for designing functional pressure sensitive devices, without any poling or annealing treatments.

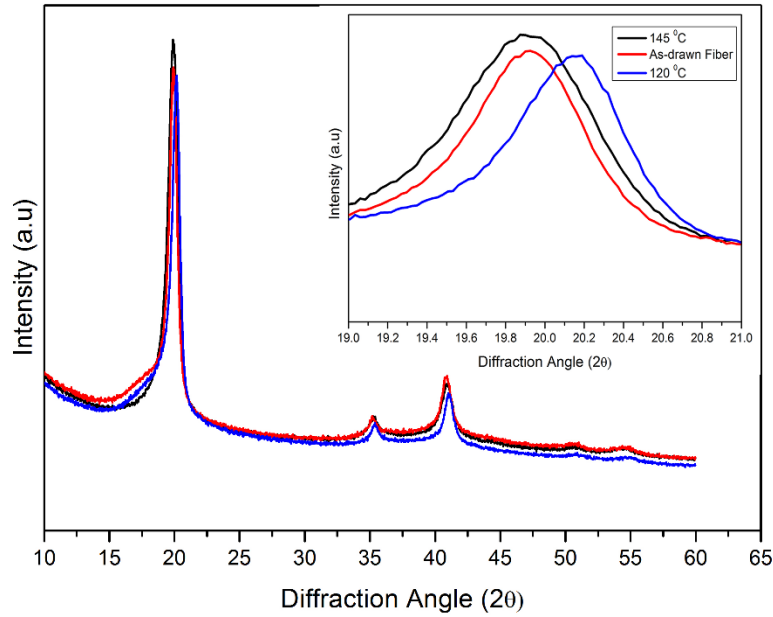


Figure 25. XRD analysis of treated and as-drawn fibers.

Next, we performed electrical characterization of annealed and as-drawn fibers. Prior to experiment, two PDMS layers were cured and cleaned with ethanol in order to get rid of the surface charges, namely triboelectric charges. 50 nm gold coated first step PVDF-TrFE fibers were sandwiched between these two uncharged PDMS layers and were contacted with copper tapes (Figure 26.a). These processes were performed on both treated and as-drawn fibers and open circuit voltage performances were compared. As demonstrated in Figure 26.b-c, the melting point temperature annealed fiber has the highest voltage responses, which is a clear proof of highest crystallinity among the other fibers. Dipoles are well oriented in that case, also as-drawn has the second maximum voltage when compared to 120 °C annealed fiber that has the lowest voltage value, which concludes that the dipole orientation is not aligned and crystallinity is minimum among the other fibers.

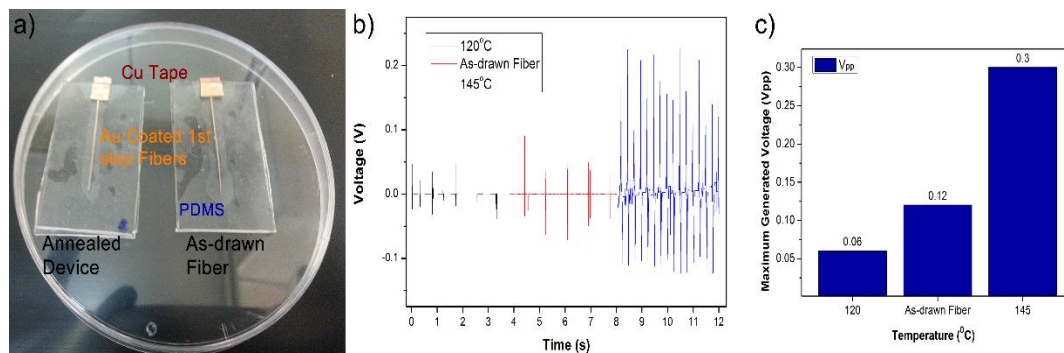


Figure 26. Electrical characterization of annealed and as-drawn fibers. a) Device structure. b) Voltage-time response of the fibers. c) Comparison of open circuit voltage values of the fiber devices.

Finally, we confirmed that crystal sizes and domain boundaries change with the annealing processes using Atomic Force Microscopy (AFM) by imaging surface topographies of each fiber. As demonstrated in Figure 27, 120°C annealed fibers have the biggest crystal size and 145°C have the minimum even in that case boundaries are nested [94]. Topographies clearly state that fiber drawing enables us to have crystalline materials and those can be controlled by annealing.

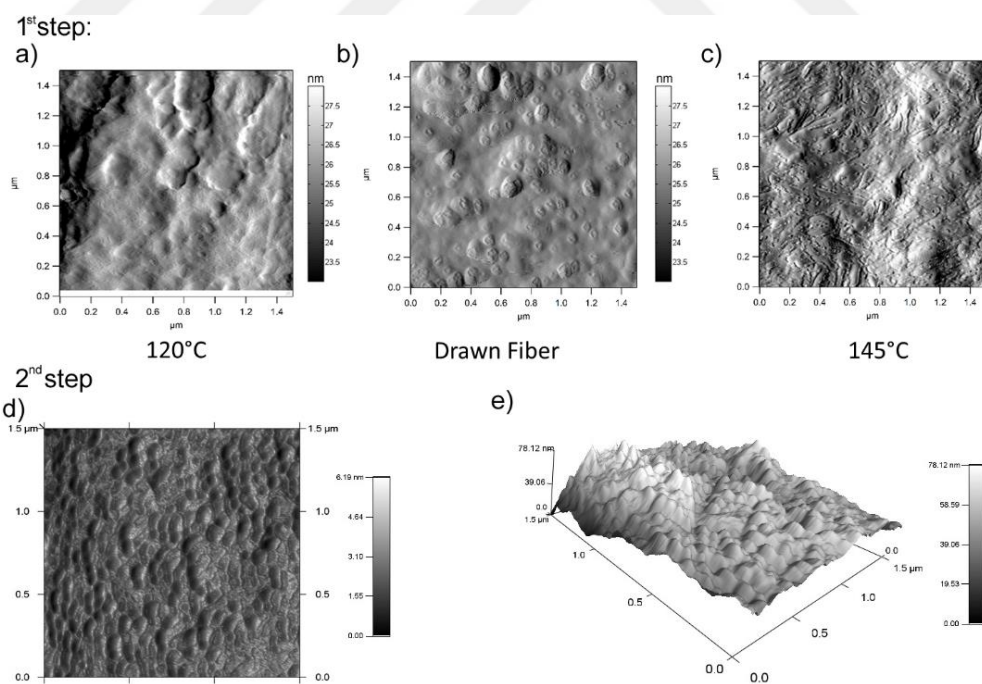


Figure 27. Surface topographies of first and second step annealed and as-drawn fibers. a, b, c) annealed and as-drawn fibers. d, e) Second step fiber surface topologies.

Chapter 3

Highly Crystalline Piezoelectric Microwires

In this chapter, the fabrication steps and phase transition analysis of the thermally drawn piezoelectric fibers are demonstrated and investigated. Highly crystalline, rectangular shape, tens of meters long PVDF-TrFE fibers, which are encapsulated in PES cladding were fabricated. The width of the core of the fibers ranges from 80 μm to 450 μm and for the second step microribbons, width ranges from 5 μm to 500 nm. XRD and FTIR analysis were performed in order to investigate the phase transition and crystallinity of the powder, bulk film and fabricated microwires. Morphology characterization of the fibers was performed with SEM. According to XRD and FTIR investigations, phase transition from non-polar alpha to beta phase was observed clearly between the bulk film and thermally drawn microwires.

3.1. New Designs to Enhance Piezoelectricity

Enhancement in piezoelectricity is becoming main focus of the producers who are designing high piezoelectric coefficient materials with electrospinning, imprinting, porous alumina templates, and thermal fiber drawing [30, 25, 53, 55]. Increasing piezoelectric coefficients let the researchers to design more stable and sensitive pressure sensors, energy harvesting applications that harvest current and voltage values in high amounts. In addition, phase transition of materials from nonpolar alpha phase to piezoelectric beta phase would increase the piezoelectricity of the polymers or the ceramics. In this study, to achieve high piezoelectric coefficients and phase transition from alpha to beta, we fabricated a thin film PVDF-TrFE copolymer with hot pressed technique, in which the temperature conditions exceeds the melting point of the material that allows us to have highly crystalline film. As demonstrated in [25], fiber drawing process could change the crystallinity and the phase of the material from bulk film to fiber. By applying the same procedures, we proved this information for PVDF-TrFE copolymer by thermal fiber drawing.

3.2. Fabrication of High Performance PVDF-TrFE Fibers

This section represents the fabrication of the piezoelectric fibers from bulk film preparation to fabrication and characterization of the PVDF-TrFE microribbons.

3.2.1. Preparation of Piezoelectric Film

Initially, we produced a film from PVDF-TrFE (Solvay Solexis 75/25) powder using an Al mold at temperature of 180 °C and 50 bar pressure (Figure 28). Hot pressing results in a perfectly homogenized and air bubble free slab. Al mold parts consists of three parts, one is a platform that holds mold together, second part is a pool for placing powder, third part is Al block for applying uniform pressure. Hot pressed film thickness is 2 mm and the width is 10 mm that fits directly into the PES preform. The film later was inserted in PES preform, which maintains hard solid structure for

drawing fiber in a controllable manner and provides cladding out of the piezoelectric film.

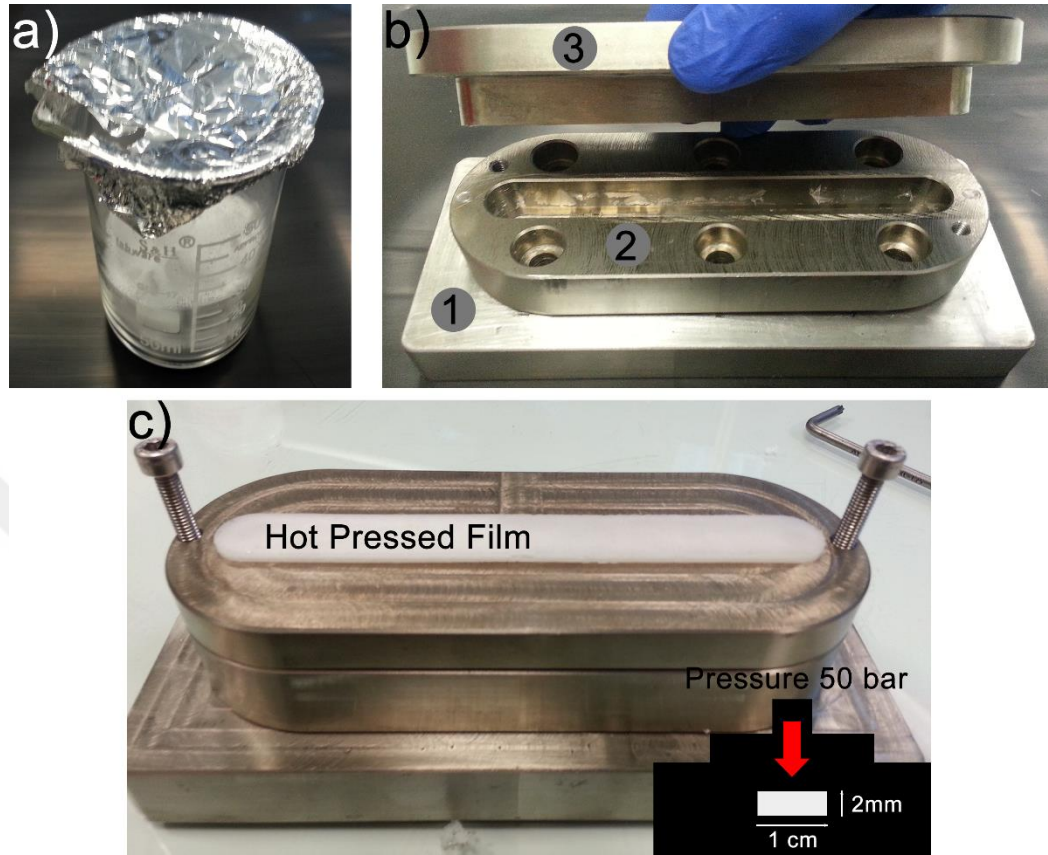


Figure 28. Illustration of PVDF-TrFE polymer slabs that we produce by a directional press. a) Powder form of P (VDF-TrFE). b) Three pieces of Al mold. c) Hot pressed piezoelectric film.

3.2.2. Preform Design

Preform fabrication process consists of three sections: first, preparation of exterior rectangular PES solid. Second, embedding piezoelectric film into backside of PES preform. Third, Consolidation process to become integrated PES preform and piezoelectric film (Figure 29).

Initially, the cover preform was prepared by rolling PES films around a 7 mm metal rod to form of a cylindrical rod. The rod is 37 mm in diameter and 26 cm in length. After the rolling of PES films, a round of Teflon tape was rolled around the preform and consolidated under vacuum condition at the glass transition temperature of the film, for a duration of 25 minutes at 240 °C. The preform becomes a solid cylindrical rod after the consolidation process. Then, the preform was machined in an industrial

turning machine to become rectangular in shape with dimension 28 mm x 32 mm. First step for preparing preform is completed with splitting solid PES structure in two halves and parts were kept in vacuum at 100 °C for two days (Figure 29 - 1). The second step is opening a channel for placing piezoelectric material, which is an important approach for multi-material fiber fabrication processes. A channel was opened to backside of the dimidiated PES preform and hot pressed PVDF-TrFE film was placed into that channel without any spacing between the PES channel and the piezoelectric film. Finally, all parts were assembled in one piece and additional PES films were rolled around the integrated PES / PVDF-TrFE structure again until the bulk composite had 28 x 28 in cross-sectional dimensions. Then, final consolidation process was performed at 240 °C for 15 minutes.

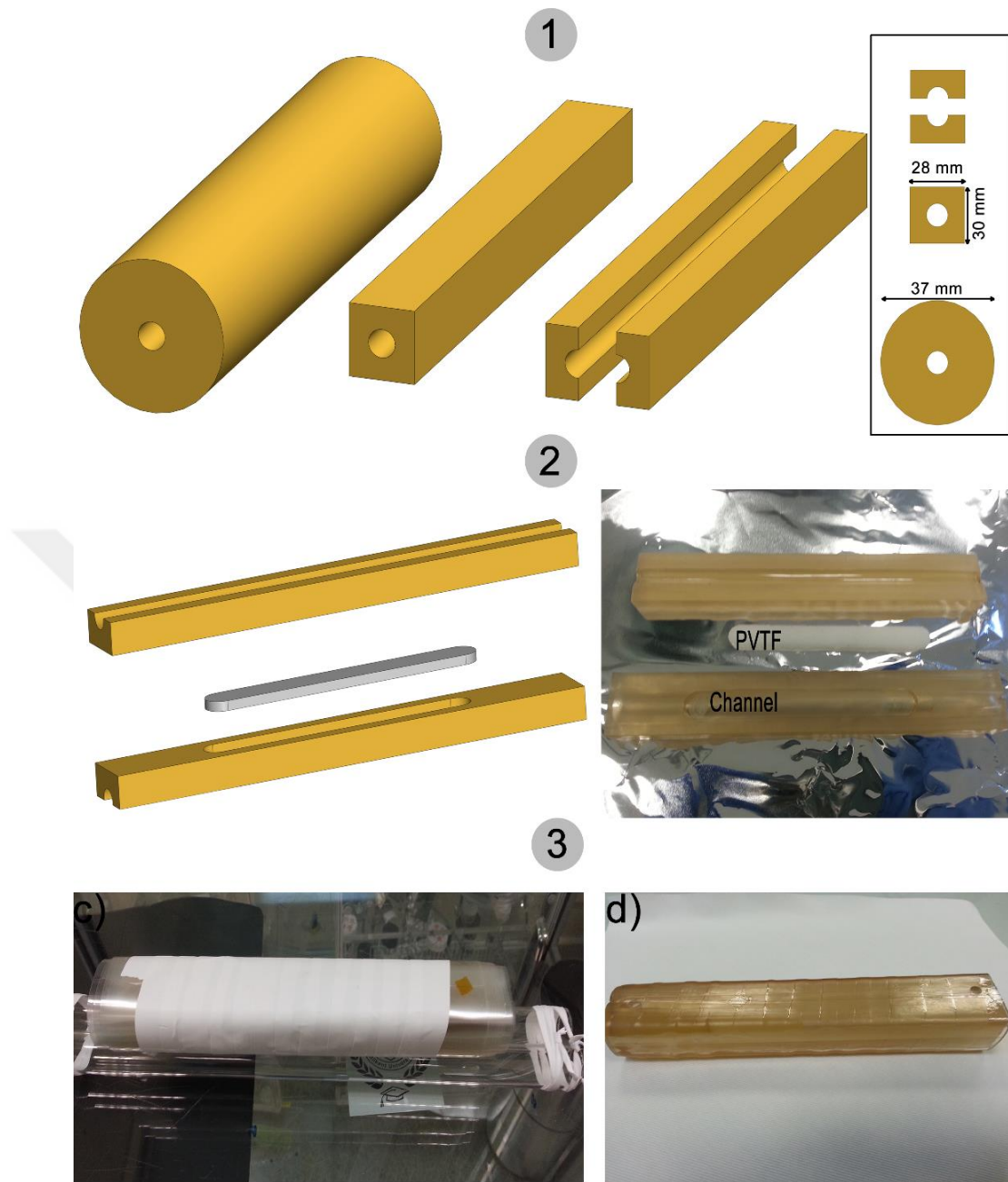


Figure 29. Fabrication steps for preform preparation. As an initial step, PES preform was fabricated that is a macroscopic copy of the cladding material (1). Inserting piezoelectric film into the PES solid (2). Final form of rectangular multi-material preform (3).

3.2.3. Fiber Drawing

Fiber drawing processes are performed in a custom made fiber tower which consists of a vertical tube oven, a preform feeding mechanism, and a real time monitoring system measuring applied stress, temperature and thickness of the drawn fiber.

Figure 30 summarizes the microribbon fabrication technique. The fabrication of PVDF-TrFE fibers starts with drawing of the piezoelectric slab embedded into PES preform. Heating the preform above the glass transition temperature of PES and melting point of PVDF-TrFE, and applying approximately MPa tensile force are required in order to trigger plastic deformation in fiber drawing process. Since drawing temperature (280 °C) or the temperature in the core of the preform (~200 °C) is higher than the melting point of PVDF-TrFE ($T_m = 145^\circ\text{C}$), the molten slab flows and shrinks in the PES cladding during fiber drawing. Fibers in thermal fiber drawing process results in PVDF-TrFE microribbons with various thicknesses by tuning applied temperature, applied stress, drawing and feeding speed.

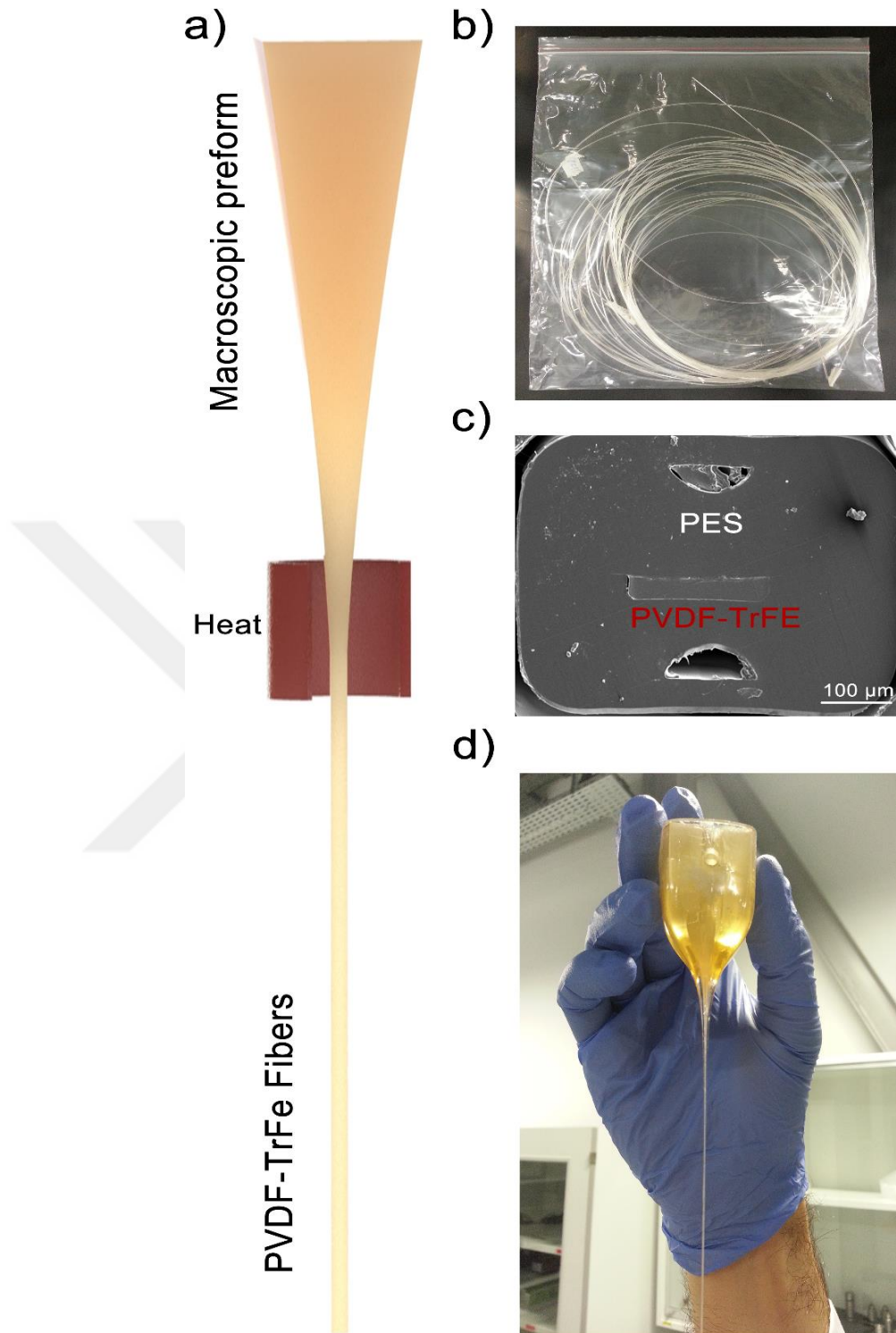


Figure 30. PVDF-TrFE fiber production. a) Schematic representation of the thermal drawing of PES / PVDF-TrFE composite preform to obtain piezoelectric microribbons. b) Tens of meters of fiber samples. c) Scanning electron microscopy (SEM) images of cross-section of fibers. d) Macroscopic residual of the preform after thermal drawing process.

During the fiber drawing process, the macroscopic form of the fiber, which is called preform was scaled down with reduction factor of about hundred. Tens of meters of fibers are drawn with variety of dimensions.

3.3. Material Characterization

Piezoelectric β phase is improved due to applied stress and temperature during fiber drawing process for PVDF-TrFE micro fibers, which were investigated using XRD (X-ray diffraction) spectroscopy, attenuated total reflectance (ATR) – Fourier transform infrared spectroscopy (FTIR) techniques and SEM characterization for morphology of the fibers. The details about the experimental setup and results are explained in the following chapters.

3.3.1. XRD Phase Characterization

XRD characterization of the PVDF-TrFE microribbons, bulk film, preform parts and bulk polymer powder samples were taken by Pananalytical X'pert Pro XRD with the diffraction angle 2θ scanned between 10 to 60 degrees by using a step size of 0.05 degrees and a dwell time 300 second per step.

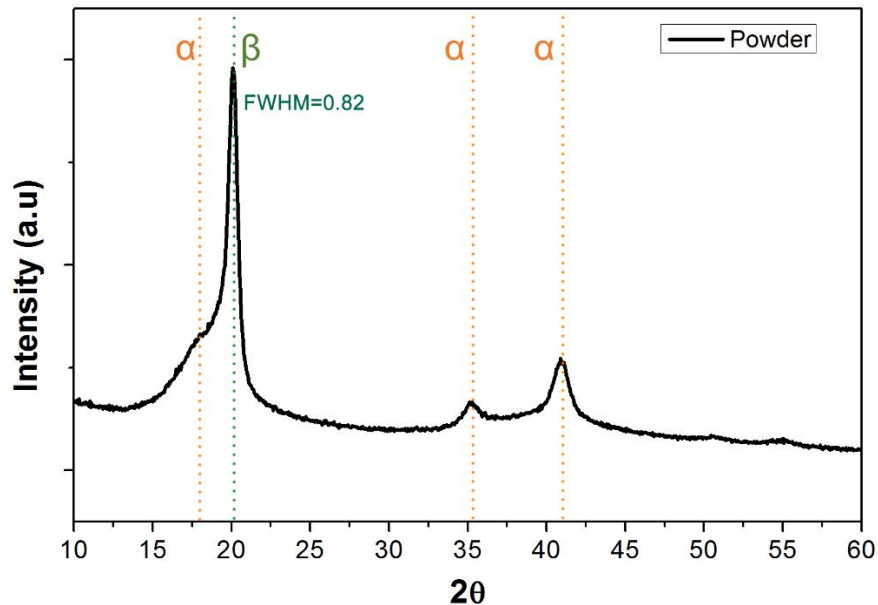


Figure 31. XRD analysis of all PVDF-TrFE powder form

Figure 32.a, b explains the phase transformation between macroscopic film (α phase) and piezoelectric fiber (β phase). From the XRD results (Fig.32), the main peak at around $2\theta \sim 20^\circ$ was from the ferroelectric beta phase with diffraction of (110) / (200) plane. The bulk film has reflections from 17.2 and 35.4 that were the diffractions from (100) and (310/020) planes, which represents nonpolar α phase [53, 90]. As demonstrated in Figure 31, the powder form of the polymer was dominated with the alpha phase, although we observed $2\theta \sim 20^\circ$ beta phase peak, corresponding alpha phase peaks $2\theta \sim 35.2^\circ$ and $2\theta \sim 40.6^\circ$ are dominant in the spectrum. The intensities of the peak at 20° increased in the case where fibers have much higher than the bulk film case (Fig.32.b), this means that the dominant phase in the fiber is the beta phase and abundance of nonpolar α reflection peaks (17.2, 35.2 and 40.6), this proves that there is a phase transition from α to β in fiber drawing process that concludes high piezoelectricity can be achieved by thermal fiber drawing. In addition, full width half maximum (FWHM) values of each beta peak proves that the crystallinity of the materials increases when the FWHM of the materials decreases in the spectra [90].

In addition, when we applied annealing to thermally drawn fibers, we observed enhancement and decrement in beta phase, also phase changing to alpha phase (Fig.32.c). Two different temperature values were chosen according to DSC analysis of microfibers [91, 92]. From the DSC results, 120°C is the Curie temperature, where crystals are not aligned perfectly in that conditions. 140°C is the melting point of the PVDF-TrFE fibers, in that conditions material is more crystalline. From the XRD result, 120°C applied fiber has the smallest intensity at 20°C reflection and has 17.2 reflection due to incomplete crystallization, which is a sign for nonpolar alpha phase. 140°C applied fiber has the highest intensity at $2\theta \sim 20^\circ$ among the others that shows that dominant phase is beta. As-drawn fiber also had a peak at $2\theta \sim 20^\circ$ corresponding to beta phase, but we didn't observe any amorphous peak from XRD study.

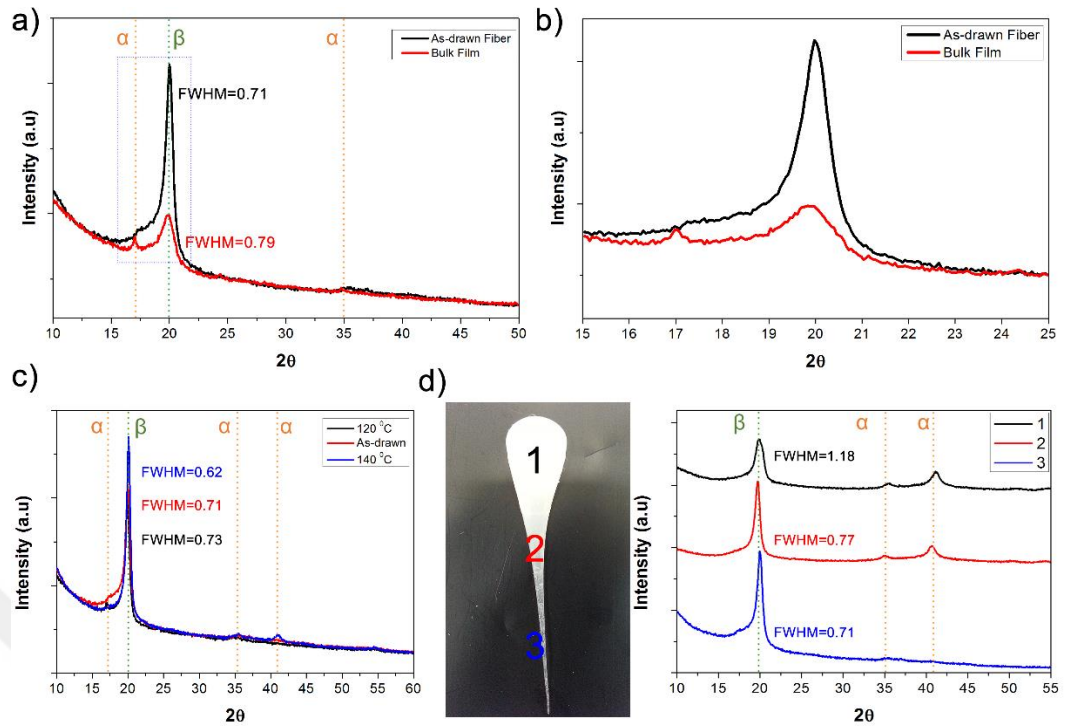


Figure 32. XRD analysis of all PVDF-TrFE samples that were involved in fiber drawing process. XRD patterns of as-drawn and bulk film (a), Magnified image of XRD spectra at $2\theta=20^\circ$, which corresponds to the piezoelectric beta phase (b), XRD patterns of annealed fibers that presents the degree of crystalline of the fibers, which are treated with different temperature values that correspond to the Curie (120°C) and melting (140°C) points of the piezoelectric material (c), XRD spectra of the preform that was left from the fiber drawing process, phase transition from alpha to beta was represented (d).

In order to understand phase transformation mechanism deeply in fiber drawing process, we performed XRD analysis for remaining drop of PVDF-TrFE film as seen in Figure 32.d. Remaining drop was divided into three sections. In section 1 and 2, nonpolar alpha peaks ($2\theta\sim 35.2^\circ$ and $2\theta\sim 40.6^\circ$) were observed in both bulk section and the transition between bulk and the fiber section. In fibers we observed ferroelectric beta phase ($2\theta\sim 20^\circ$), which has the maximum value amongst other sections.

3.3.2. FTIR Characterization

Another tool that we used to analyze phase transformation of microribbons is Fourier transform Infrared Spectroscopy (FTIR) with an ATR attachment (Thermo Scientific Nicolet iS10). FTIR transmission data were taken with a wavelength scan

resolution of 0.482 cm^{-1} and a total of 128 scan steps, the wavelength interval is between 600 and 1600 cm^{-1} bands [53].

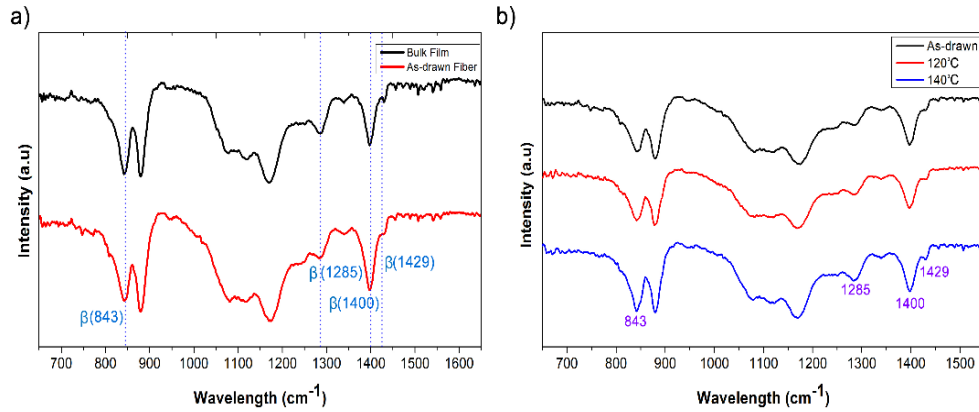


Figure 33. FTIR spectra analysis of the as-drawn, thermally annealed fibers and the bulk film under the light is polarized perpendicular to the direction of the fiber drawing. (a) FTIR spectra of the bulk film and the as-drawn fibers, beta phase is dominant. (b) FTIR spectra of the thermally treated fibers, beta phase is dominant.

ATR-FTIR results are demonstrated at Figure 33, the polar beta phase peaks appeared at 840 , 843 , 1285 and 1429 cm^{-1} for both fiber and bulk film. Nonpolar alpha phase 612 , 765 , 796 , 854 , 870 , 970 cm^{-1} were not observed for all samples. One of the strongest peak at 840 and 843 cm^{-1} can be referred to symmetric stretching bands of C-F and C-C bonds. Similarly, the peak at 1285 cm^{-1} defined for symmetric C-F and C-C stretching and symmetric C-C bending. The peak at 1429 cm^{-1} referred for symmetric C-H bending [30, 53]. For temperature treatment case, we didn't observe any peaks corresponding to alpha phase. All temperature treated (annealed) fibers and as-drawn fibers represent perfectly β phase (Figure 33.b).

3.3.3. Morphological Characterization

PVDF-TrFE fibers were studied for morphological characterization by using scanning electron microscopy (SEM). Figure 34 represents cross sectional and longitudinal SEM images of $400\text{ }\mu\text{m}$ thick microribbon embedded fibers. We extracted PVDF-TrFE microribbons out of the PES cladding using mechanical extraction or etching in DCM, which can't dissolve P (VDF-TrFE). SEM images are taken using FEI Quanta 200 FEG Electron Microscopy with low voltage – high contrast detector

under vacuum at 6×10^{-5} Pa chamber pressure. We used 10 kV acceleration beam voltage within 10 mm working distance. Cross-sectional characterization of nanoribbons requires a special sample preparation using ultra-microtome for SEM imaging. Firstly, fibers were embedded in a resin (Technovit 7100). After, using Leica EMUC6 – EMFC6 Ultra-Microtome with a diamond knife, fiber cross-section cut is performed. Before SEM images, 5 nm Au/Pd was sputtered on the smoothed surfaces.

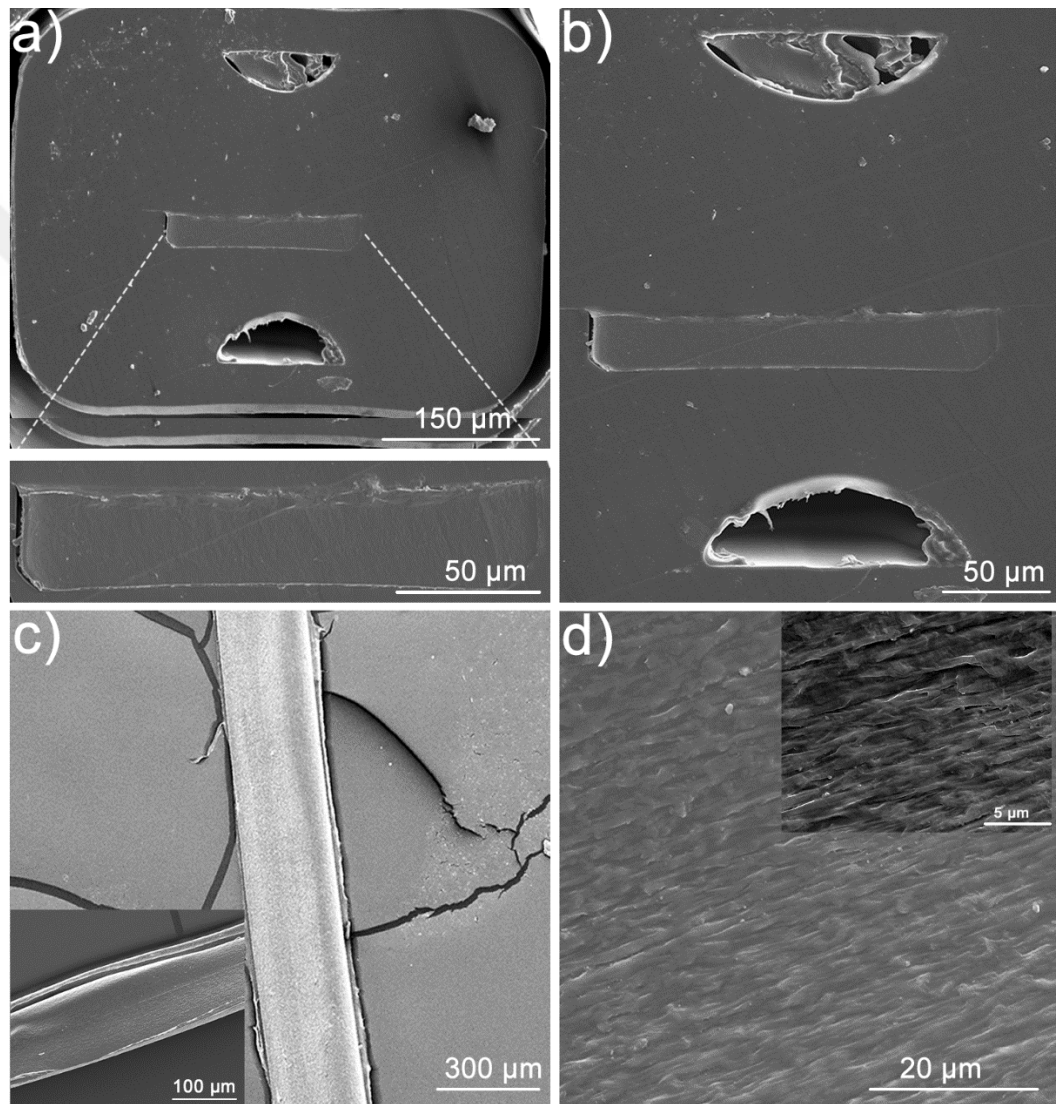


Figure 34. SEM micrographs of PVDF-TrFE micro fibers produced by thermal fiber drawing. a) Cross-sectional of the piezoelectric fiber in the PES cladding. b) Magnified image of (a). c) Lateral image of extracted fiber. Inset: Etched fiber. d) Closer look at the microribbons that shows the piezoelectric film layers.

3.4. Iterative Fiber Drawing

For size reduction in PVDF-TrFE fibers one step of thermal fiber drawing is applied that bridges the macroscopic and the nanoscopic world. The fabrication of PVDF-TrFE several micron and sub-micron fibers, which comprises of additional fiber drawing step, starts with the drawing of PVDF-TrFE film embedded in PES preform. Millimetric fibers obtained from the first thermal size-reduction step were cut and arranged in hexagonal lattices inside a protective jacket, vacuum consolidated and redrawn. Figure 35 summarizes the fiber fabrication.

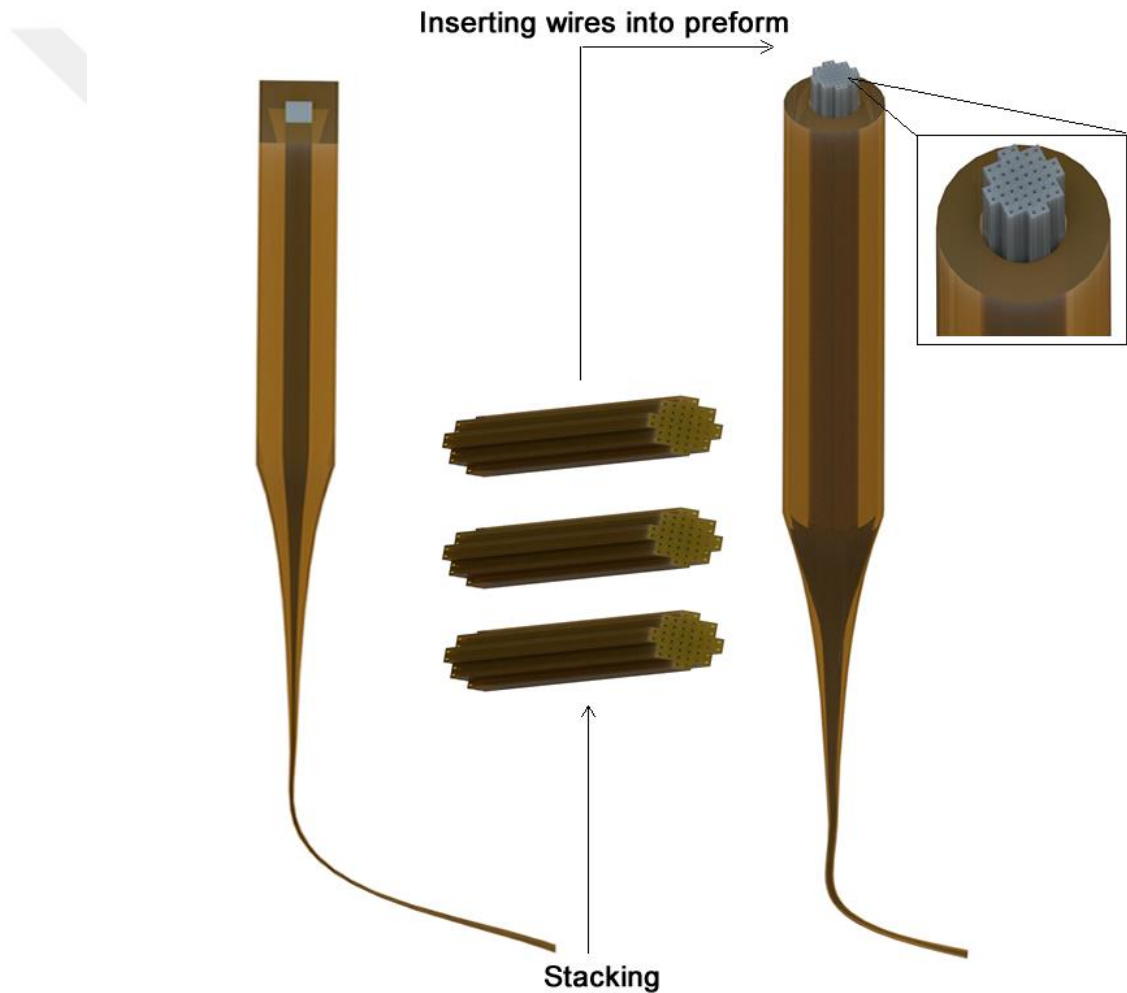


Figure 35. Schematic representation of iterative size reduction technique for PVDF-TrFE fibers.

The thickness of the ribbons ranges between 500 μm to 80 μm in the first step, 5 μm to 500 nm in the second step. Approximately, 85 fibers were used in the second step fiber drawing.

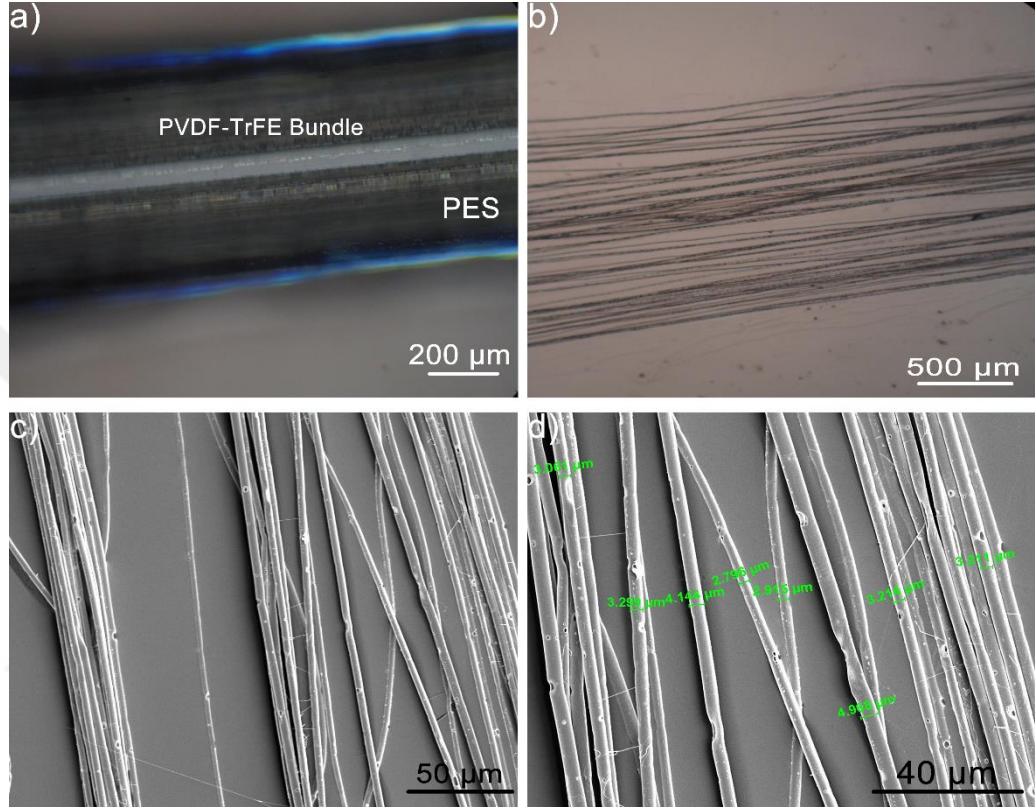


Figure 36. Optical and SEM micrographs of PVDF-TrFE microribbons. a) Optical image of PVDF-TrFE microribbon array embedded in PES cladding. b) Optical image of second step PVDF-TrFE microwires extracted out of their cladding. c-d) SEM images of second step fibers.

We extracted PVDF-TrFE microribbons out of the PES cladding by etching in dichloromethane (DCM), which cannot dissolve PVDF-TrFE. Additionally, a better SEM observation of the ribbon shape is accomplished by breaking the fibers after a liquid nitrogen treatment. Figure 36 and 37 demonstrates the morphological characterization and the images of the microribbons by optical microscope and SEM.

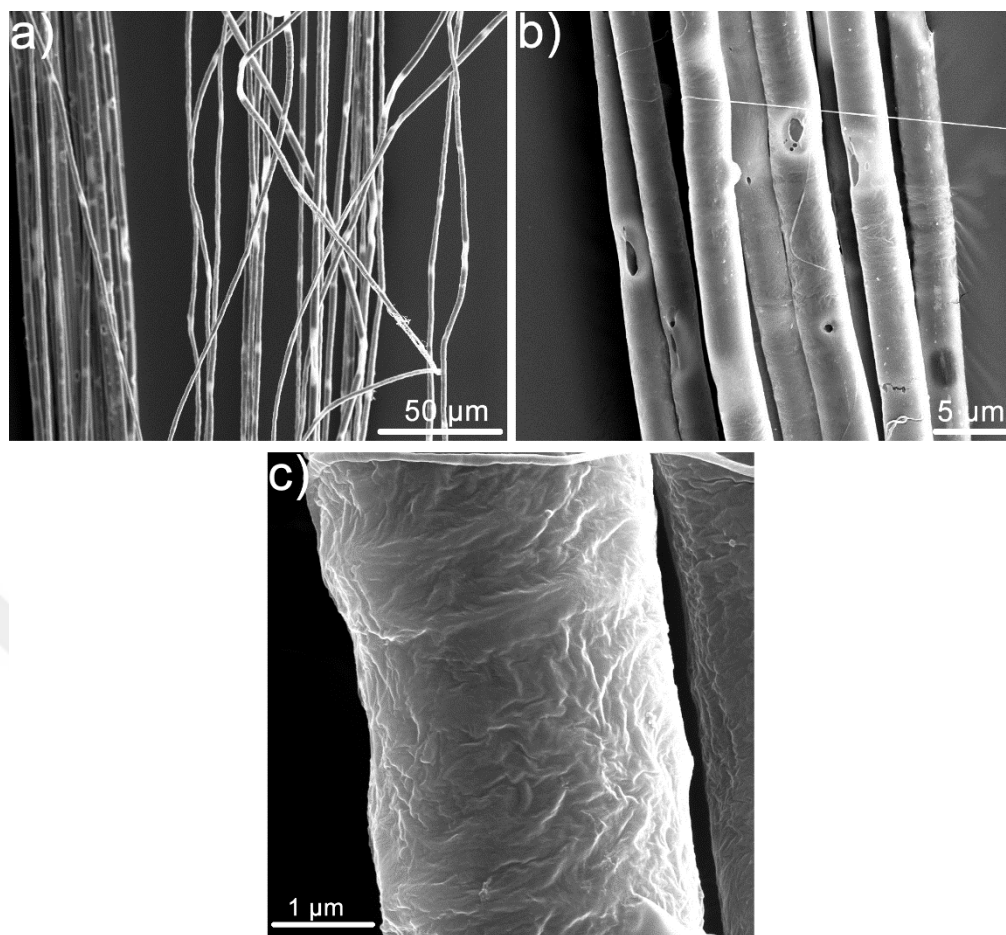


Figure 37. SEM images of the second step microribbons for morphological characterization. a) SEM images of arrays of PVDF-TrFE microribbons. b) Magnified image of the rectangular shape PVDF-TrFE fibers, approximately 2-4 μm in width. c) A closer look at the PVDF-TrFE microribbons that shows the crystallinity and the shape preservation of the material.

Chapter 4

Conductive Polymer/CNT Composite Films and Fibers

A flexible, stretchable and conductive polymer/carbon nanotube (CNT) composite film, micro and nanofibers that can be used as flexible interconnects and for energy storage applications are fabricated and characterized. We optimized a composition of Conductive Polyethylene (CPE) and metallic MWCNTs by dissolving in Xylene and prepared a thin film nanocomposite with a uniform $\sim 10^3$ S/m conductivity. Further, we applied three steps of thermal fiber drawing in order to produce micro and nanowires by using nanocomposite film and cladding polymer. Morphological characterization of the composite film and fibers were performed in order to observe distribution of CNT in the polymer matrix.

4.1. Introduction

Flexible and stretchable nanocomposite conductors have been used in a wide range of applications such as conductive substrate for active matrices, printed electronic circuits, pressure sensors, biomedical devices and energy applications [11, 62, 95-98]. Nanomaterials have superior electronic and mechanical properties, large surface areas and recently, compatible with the fabrication processes. Dispersion of one-dimensional nanomaterials such as carbon nanotubes (CNT), metallic nanowires and nanoparticles in the elastomeric substrates (mostly polymers), enhances the composite conductivity while the mechanical properties are preserved or improved [99]. One of the effective method to create nanocomposites is that embedding one dimensional nanomaterials such as CNTs, silver and copper nanowires or nanoparticles and 2D material graphene [95, 100-103]. Although the filler material property is crucial in evaluating the composite performance, host material namely substrate properties such as stretchability, elasticity and flexibility, which mainly brings Polydimethylsiloxane (PDMS) to the production line. However, different attributes of alternative stretchable materials, for instance elastomers (rubbers), gels, conductive polymers (polyaniline, polyurethane etc.) and organic semiconductors have been utilized to design functional composites that have predominant properties against the PDMS based nanocomposites [98, 104-107]. With decent combination of these functional fillers and elastic materials, highly conductive and flexible composites can be designed for flexible and stretchable electronics applications [99-108, 109].

Due to their sizes, high aspect ratios, high surface area, outstanding mechanical and electrical properties, carbon nanotubes are excellent fillers for the conductive composites. Dispersion of both single and multiwalled CNTs in the polymer matrix improves the overall conductivity performance of the composite where the whole structure is still flexible and stretchable. There are two ways to prepare CNT/polymer composites by dispersion of nanotubes. In the first approach, CNTs are dispersed in a solvent by mixing or ultrasonication and then CNT/solvent can be dispersed in the polymer. Alternatively, nanotubes can be dispersed in both polymer/solvent mixture. There are several types of composite couples in the literature such as CNT/elastomer composites, and CNT/conductive polymer composites [110, 111]. The conductivity

values are ranging in these fabrication types of composites from 0.1 S/cm to 102 S/cm [99]. A CNT/rubber composite was demonstrated in [95], in which nanotubes were dispersed in the ionic liquid and embedded in fluorinated copolymer and the composites shows the conductivity values of 57 S/cm. There are many PDMS/CNT composites that have been demonstrated in the literature and shows PDMS as an excellent candidate for the host flexible substrate. SWCNT - aerogel / PDMS elastic conductor composite [106] has the conductivity of 1.08 S/cm. Several elastomer composite values can be listed accordingly, MWCNT/PDMS composite [114] 10^{-5} S/cm, cross-stacked super-aligned MWCNT film/CNT [115] 63 S/cm, doped CNT film/PDMS [62] 1100 S/cm, respectively. A wide range of polymers can be used in polymer/CNT composites. Some of the most common polymer nanocomposites produced by dispersion of carbon nanotubes in the polymer matrix are polycarbonate (PC) [116], polyaniline (PANI) [28, 98, 117, 118] with conductivity ranges 0.1-10 S/m, Polyurethane [117] 0.5 S/m. These polymer composites ratios, weight percentages from 0.02 %wt to 3% wt. Many models, various functionalization, fabrication approaches and material couples for CNT/polymer composites are demonstrated and tabulated, in addition various applications such as, flexible electrodes, substrates, electronic papers and aerospace industries [112, 113].

A fabrication technique, which is capable to produce extreme high aspect ratio, well-ordered, highly conductive, flexible, stretchable and high elastic modulus, is demanded. We developed a promising MWCNTs / carbon loaded polymer nanocomposite material for flexible electronics based on thermal size reduction method. Initially, we optimized composition of Conductive Polyethylene (CPE) and metallic CNTs by dissolving it in Xylene and prepared a thin film nanocomposite with a uniform $\sim 10^3$ S/m conductivity. Further, we fabricated a bulk rod using our conductive films for processing it through three steps of size reduction process, which is based on thermal fiber drawing technique [23]. We obtained kilometer long, conductive, ordered, flexible, stretchable micro and nanowires with 300 - 800 μm , 2 - 8 μm and 50 - 300 nm in diameters in step 1, step 2 and step 3 fiber drawing process, respectively. Raman Spectroscopy, SEM, and TEM investigations, four probe conductivity measurements were performed in order to characterize prepared the films and micro and nanofibers.

4.2. Material Characterization

Microscopy and spectroscopy techniques are performed for CNT, conducting polymer CPE and composite material characterizations. Electrical and mechanical performance of composite film and fibers were also performed for demonstrating their possible applications in flexible electronics.

4.2.1. CNT Characterization

For characterization of metallic multi-walled carbon nanotubes, both microscopy and spectroscopy techniques are used. Scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM) were performed in order to analyze form, morphology and shape of the nanotubes.

SEM allows us to analyze CNT structures and forest both in nano and micro scale. An environmental (FEI Quanta 200F) SEM was used to observe CNT forests and bundles. Small quantities of MWCNT were mounted on a SEM stub, which is connected them with a copper tape. Since the nanotubes are conductive, we did not perform sputtering gold on to nanotubes. Parameters for imaging CNTs: accelerating voltage: 5-10 kV, a spot size of 3 μm and working distance of 10 mm. Images of MWCNTs are demonstrated in Figure 38a and 38b. Bundles of 5 μm MWCNTs can be observed easily and they form a CNT forest without dispersion in any environment.

A TEM (FEI TECHNAI F30) was used to observe structure, size and homogeneity of carbon nanotubes. MWCNT samples were dispersed in ethanol, a drop of mixture was placed on grip and images were recorded. TEM images of 5-6 walled carbon nanotubes were recorded and diameter of each nanotube was measured as 12 nm in length of several micrometers. TEM images are illustrated in Figure 38.c-d.

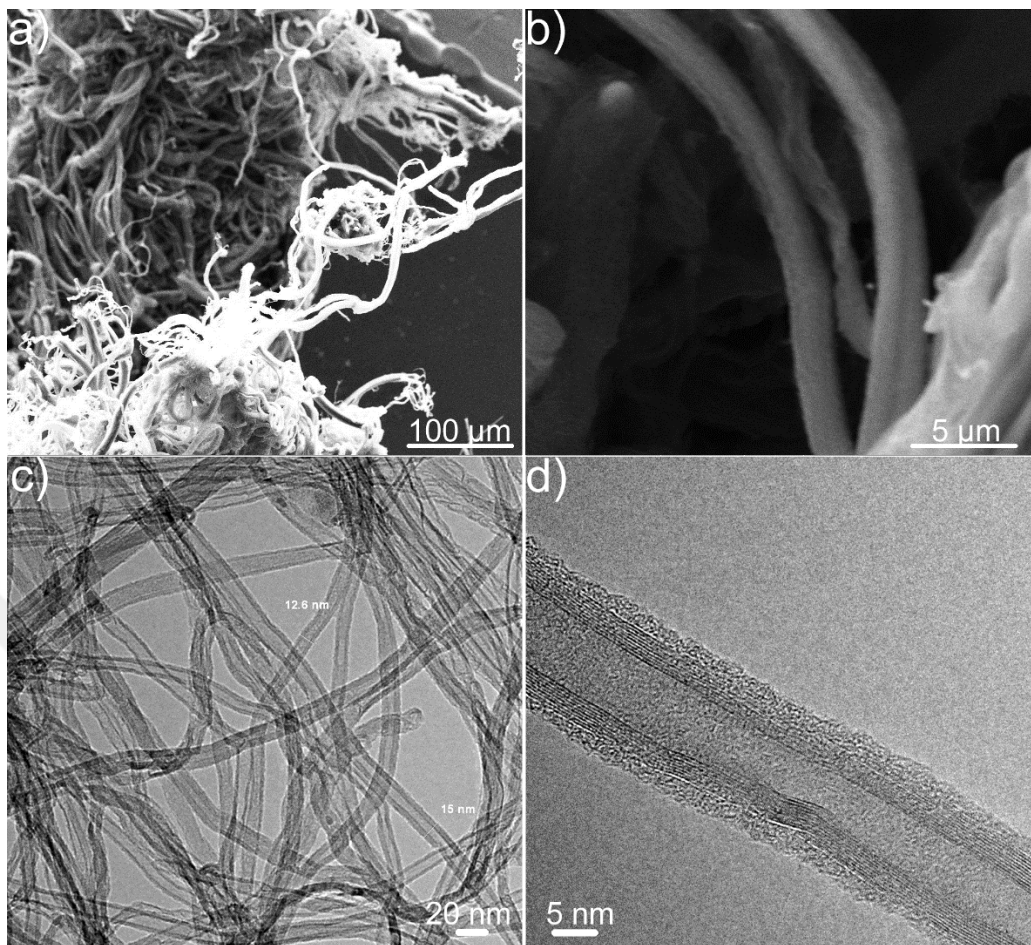


Figure 38. SEM and TEM images of MWCNTs. a) SEM image of MWCNT forest. b) SEM image of CNT bundles. c-d) TEM images of MWCNT.

4.2.2. Conductive Polymer Characterization

Carbon loaded or conductive polyethylene (CPE) is an industrial level polymer whose the material is loaded with extra carbon, which enhances the overall conductivity of the material. However, its conductivity is limited, therefore CNT addition would improve its conductivity without any damage its original structure. In order to understand polymer's thermal behavior, which gives an idea for consolidation and fiber drawing temperatures DSC and TGA characterization techniques were used.

Dynamic differential scanning calorimetry analysis was performed by using DSC Q2000 (TA Instruments) under nitrogen atmosphere, weighing of samples are 4-5 mg. Melting point of the polymer is around 110 °C, which is illustrated in Figure 39.a. This experiment was performed in order to choose cladding polymer for the fiber

fabrication process. Thermo-gravimetric Q500 (TA Instruments) analysis was used to determine the phase transition point of the conducting polymer CPE. The polymer has a good thermal stability up to 350 °C. The decomposition temperature of the polymer is around 500 °C. Figure 39.b shows the thermogram of the polymer.

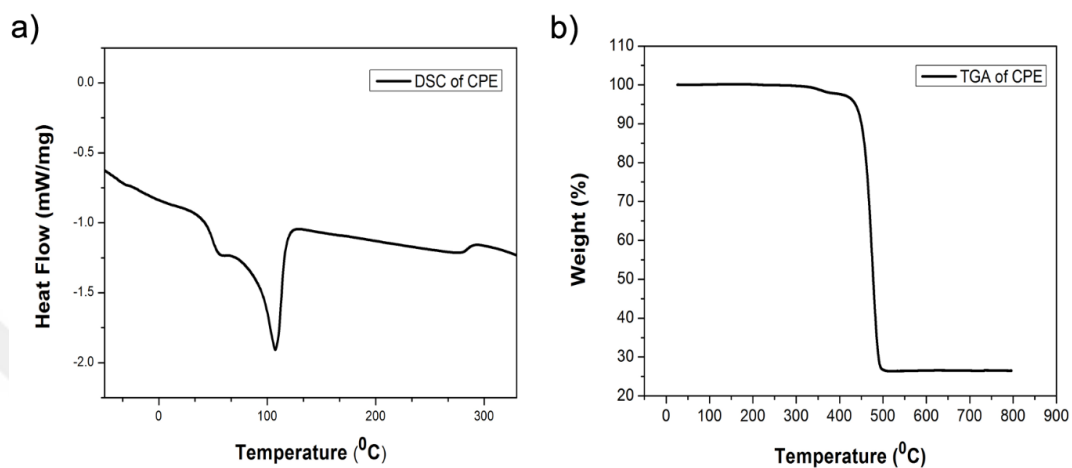


Figure 39. DSC and TGA analysis of CPE polymer.

Mechanical performance of the polymer was characterized by tensile test. 5 x 1 cm polymer was gripped in Universal Testing Machine (Instron - Model 5969), in order to analyze mechanical strength of the film. Figure 40 demonstrates the stress- strain curve of the polymer, inset: image of the setup. The stretchability of the polymer exceeded 350% under the tensile strain, which shows that the material can be used in flexible and stretchable electronics applications.

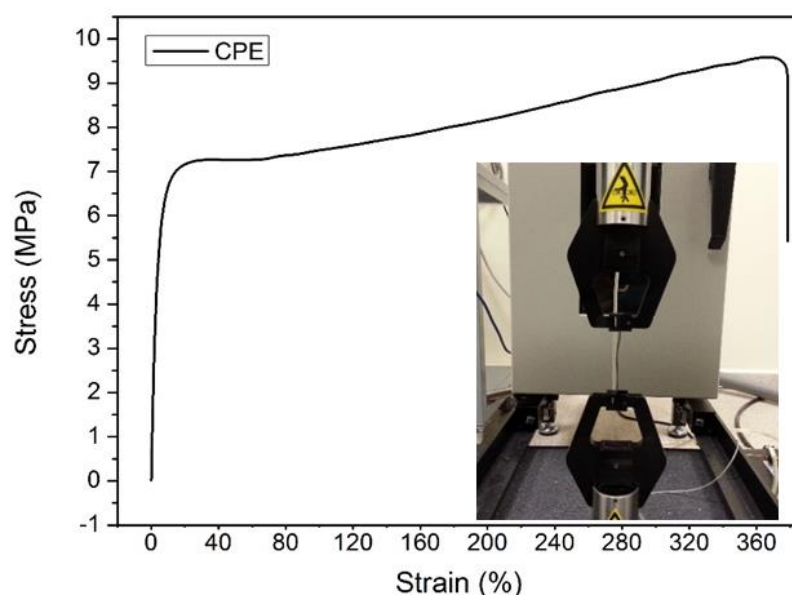


Figure 40. Mechanical characterization of CPE which corresponds the flexibility and stretchability of the conductive polymer.

Electrical conductivity performance of the film was also measured, which is 5 S/m in bare form. This value was increased by addition of nanotubes in the polymer matrix. Calculations and experiments regarding conductivity issue will be given in next sections in this chapter.

4.3. CPE/CNT Blend Fabrication and Characterization

As presented in Figure 41, fabrication of elastic CPE/CNT film consists of several steps. Prior to fabrication of the film, carbon nanotubes are needed to be processed. Firstly, MWCNTs were dispersed in ethanol solution to ratio of 1:8 by bath sonication for 30 min. Next, ethanol was vaporized from the mixture and remaining CNTs were annealed in vacuum furnace at 300 °C for 24 hours in order to get rid of the residual materials and hydrogen bonding.

To make a composite film, processed 40 mg of CNTs, 2 grams of CPE and 20 ml of Xylene were mixed under the conditions of 80 °C for 5 hours with magnetic stirring. Mixing step is important to disperse CNTs into polymer matrix. Afterward, mixture was drop casted in a Petri dish and the dish was shaken for 20 minutes. The film was air dried for 3 days to remove Xylene solvent in fume hood. The bulk film was then hot pressed in between two aluminum 6x6 cm layers in 100°C for 3 minutes, for

preventing stacking the composite onto Al plate thin layers of Teflon films that were used to cover on plates. The final form of the film has the thickness of 200 μm and square shape.

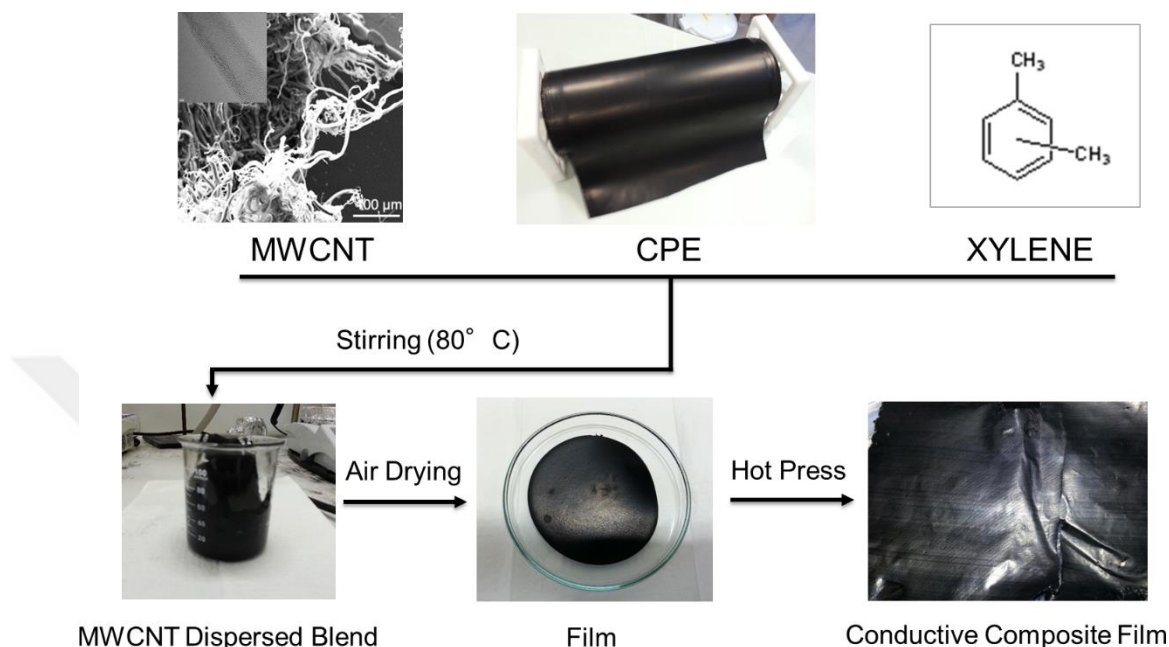


Figure 41. Schematic representation of MWCNT/CPE blends. Materials and film casting technique is represented.

2 %wt of composite films were fabricated in order to have elastic, flexible and conductive substrate. This weight percentage was chosen because after 2%wt of the mixture the nanotubes were not dispersed well enough inside the solvent and the polymer starts precipitating in glass beaker, therefore uniform films cannot be obtained.

Composite film characterization was performed by SEM, Raman spectroscopy and conductivity measurements, which will be mentioned in the next subsection.

SEM images were obtained 2 wt% MWCNT/ conductive polymer CPE composite to observe the dispersion of nanotubes in the polymer matrix and morphology of the composite films. As demonstrated in Figure 42, MWCNTs were dispersed randomly in the polymer matrix. Bundles of carbon nanotubes are located at several points on the CPE and overall distribution enhances conductivity. Images are taken from both composite film and the preform inside the PC tube.

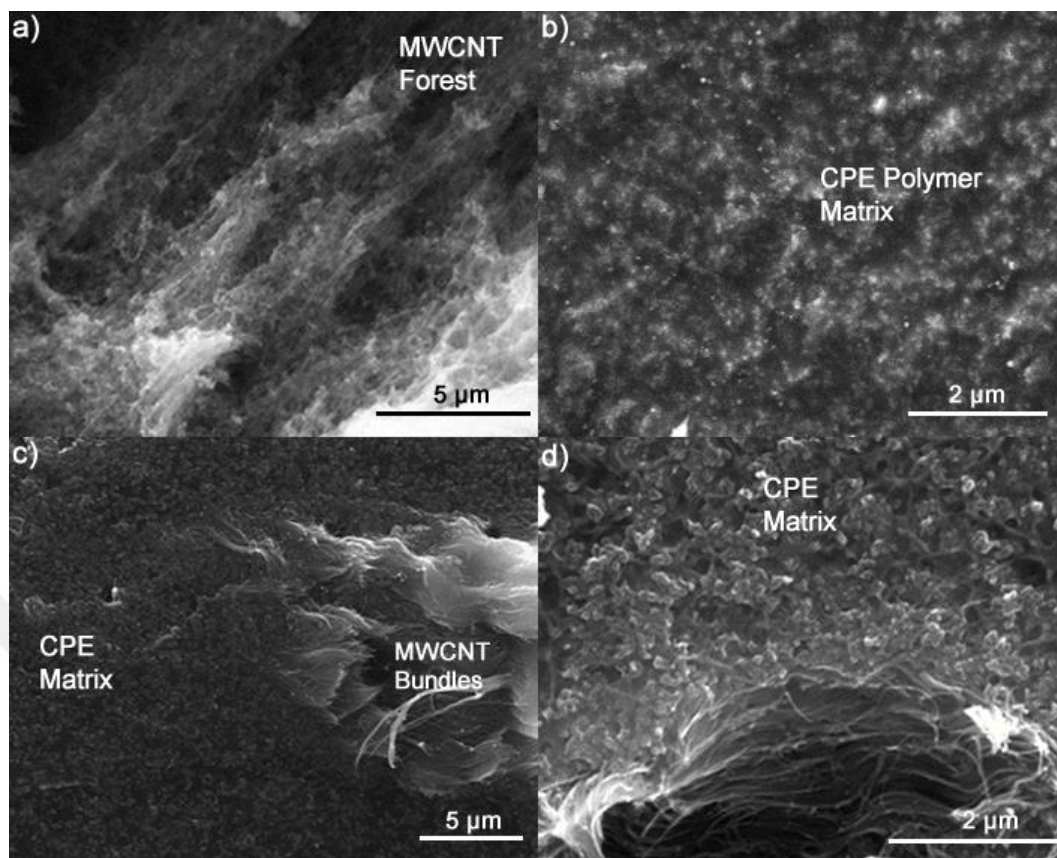


Figure 42. SEM images of CNT, conductive polymer and composite. a) SEM image of MWCNT. b) SEM image of conductive polymer. c-d) SEM images of MWCNT/CPE blends with different scale bars.

Raman spectroscopy is a powerful technique for characterizing carbon based materials such as carbon nanotubes and graphene. The diameter of nanotubes, carbon bonds (sp^2) as well as specific carbon bands can be examined by this technique. Polymer/CNT based composite materials have been differentiated using Raman spectroscopy by changes in peaks or the wavelength shifts in the spectrum.

Here, we performed Raman spectroscopy in order to identify characteristic peaks of the MWCNT and differentiate peaks changes and shifts for the polymer, composite film and the thermally drawn fibers. The Raman spectra was recorded Near-field scanning electron microscopy (SNOM) in conjunction with confocal Raman microscope with a light source Nd: YAG laser wavelength of 532 nm, focused on the materials with a 50x objective.

Initially, raw carbon nanotubes were dispersed in ethanol solution by ultrasonication for 20 minutes and Raman spectrum experiment was performed after

casting the mixture on a glass slide and evaporating of the solvent. As shown in figure 43.b, the two typical graphite bands are observed in the spectrum of the MWCNT forest: the band at 1580 cm^{-1} is called G band that peak is assigned to the vibration of C-C bond, we also observe a band around 1350 cm^{-1} , which is known as D band, coming from the defects or disorders on the structures [120]. The spectrum also exhibits a band at around 2700 cm^{-1} , called as G' band, this band was attributed as overtone of the D band.

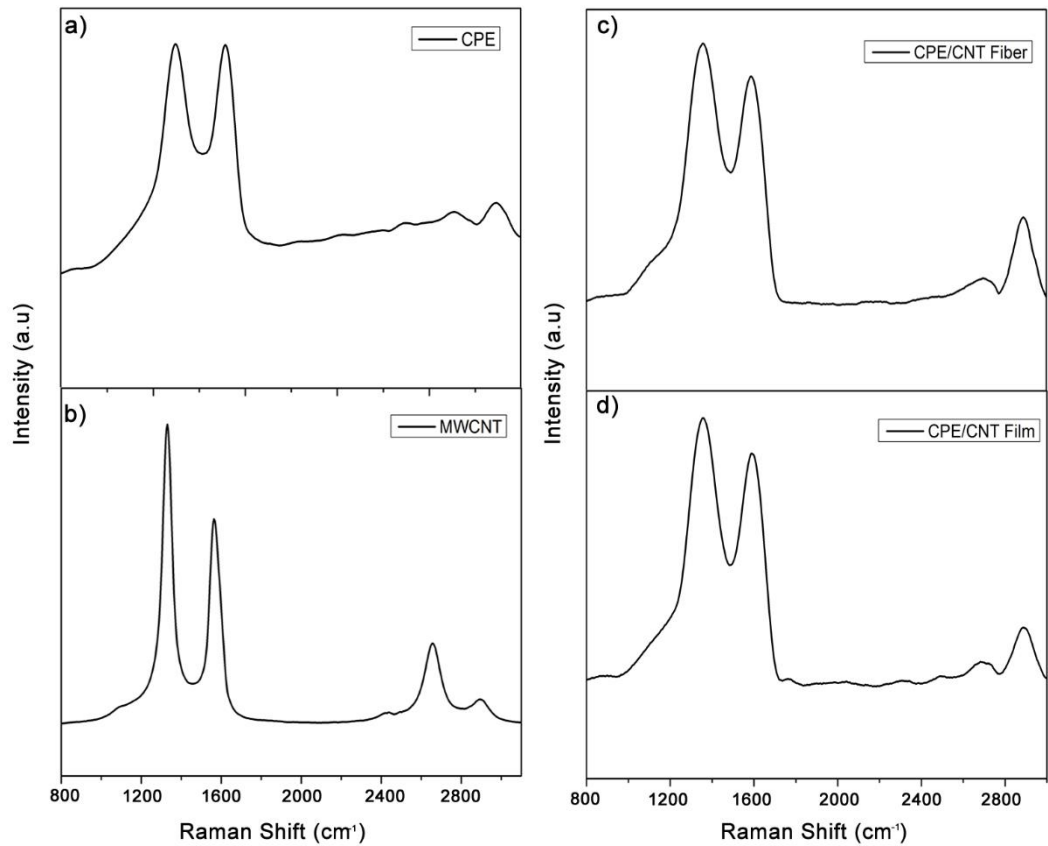


Figure 43. Raman spectra of carbon loaded polyethylene (CPE). (a) ,unfilled CPE (b), second step composite fiber (c), 2 %wt composite film (d).

Figure 43 displays the Raman spectrum of the bare polymer, 2 %wt composite film and second step fiber. For composite film and fiber case, nanotube peaks can be observed, also peaks from the polymer were dominant because of the random distribution of nanotubes in the polymer matrix.

4.4. Electrical Characterization

Direct current (DC) resistivity is an important electrical characterization for polymer/CNT composites that defines the material whether it is conductor or an insulator [21, 62]. Here, we performed four-point probe resistivity measurements with a custom made four point probe station. As illustrated in figure 44, a current is passed through the outer probes and this current induces a voltage in the inner voltage probes. These four probes, which are made from metal, were connected a source meter (Keithley 2400 Sourcemeter) that calculates the surface resistivity of the material from the basic Ohm's law equation($R=V/I$). The four point probe system typically used to determine bulk resistivity of the materials. Resistivity is calculated from the formula:

$$\rho = \alpha \frac{V}{I} t \quad (7)$$

where, ρ is the resistivity, V/I is the value that is read from the source meter, t is the thickness of the material, α is a constant value of 4.53.

Conductivity is the reciprocal of the resistivity, from the relation $\sigma=1/\rho$, conductivity of the materials can be calculated.

For our experiments, bare CPE and CPE/CNT composite films were placed under the four probes where the probes and material were in contact. Then resistivity values were read from the screen of the source meter. Fundamental equations were calculated.

Unprocessed CPE, $R= 320 \, \Omega$, $t=0.15 \, \text{mm}$,

$$\rho = (4.53 \times 320 \times 0.15 \times 10^{-3}) = 0.217, \quad \sigma = \rho^{-1} = 4.6 \, \text{S/m}$$

CPE/CNT Film, $R=8 \, \Omega$, $T=0.05 \, \text{mm}$,

$$\rho = (4.53 \times 8 \times 0.05 \times 10^{-3}) = 0.00183, \quad \sigma = 546.4 \, \text{S/m}$$

From the calculated conductivity values, our composite film is hundred times more conductive than the bulk material. This value of the conductivity shows that our composite material can be used in flexible conductive electrodes also, can be used as a conductive substrate for the flexible electronics applications. In addition, we calculated composite second step fiber conductivities, micro wire conductivity values are ranging from 0.1-1 S/m.

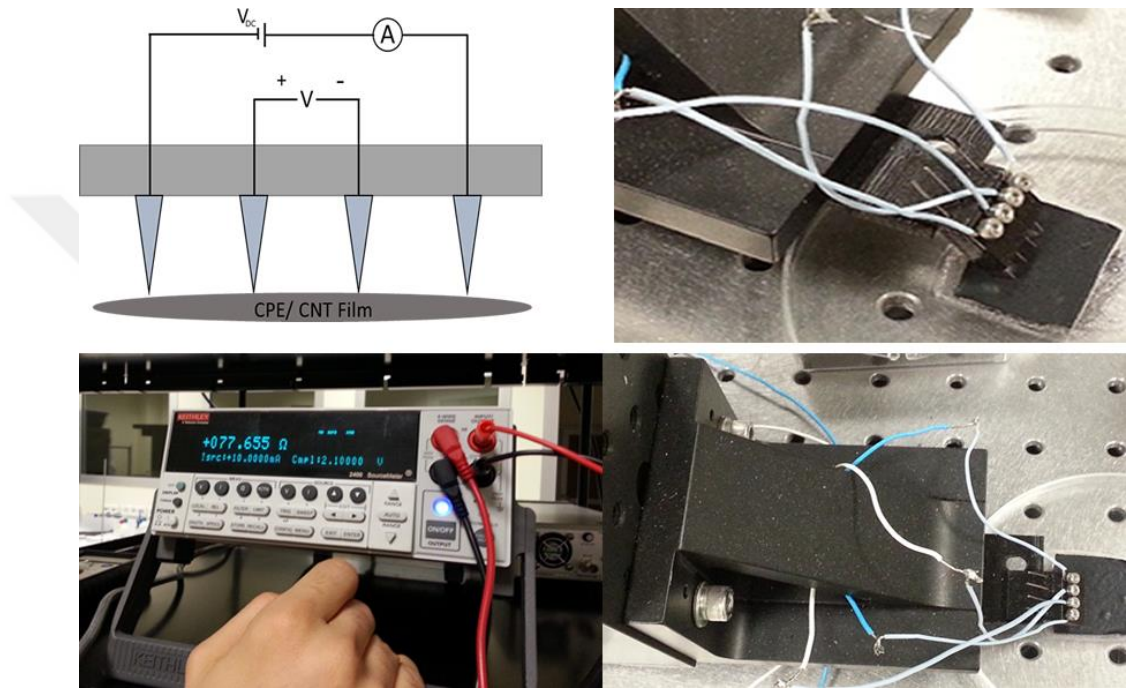


Figure 44. Schematic representation and experimental setup images of four-point probe conductivity measurements.

4.5. Fiber Design and Characterization

Micro and nanowire geometry allows us to have high aspect ratio, high surface area materials, this form of geometry brings extreme mechanical and electrical properties. For functional devices nanotubes and geometries, nanotubes, nanoribbons and nanowires should be produced in well-ordered, high density, aligned and oriented form. Iterative size reduction technique allows us to have materials that have the aforementioned properties and combine multimaterials in a single fiber array. Here, by using CPE/CNT composite, we aim to have aligned and ordered carbon

nanotube/conductive polymer arrays and to enhance the conductivity of the composite by applying thermal fiber drawing.

4.5.1. Preform Design

Preform design and fabrication is a crucial step for fiber drawing that can cause breaking off or damaging to the process. For CPE/CNT composite fiber production we choose 'rod insert tube' method. In this procedure, a tube is prepared prior to inside material production, then core material is designed and inserted in to the tube, finally two different material is combined together. For our case, initially, the cover preform was prepared by rolling Polycarbonate (PC) films around a 6 mm metal rod to form a cylindrical rod. The tube was 22 mm diameter and 16 cm in length. After, the rolling of PC films, a round of Teflon tape is rolled around the preform and was consolidated in a vacuum condition at 200°C for 30 minutes. The preform becomes a solid cylindrical rod with an inner core of 6 mm. Next, core material is prepared by designing another rod. To begin with, CPE/CNT composite film was broken into pieces of 6 mm diameter circle. These circles are embedded in glass tube and squeezed till the length of the black composite became 8 cm, then the whole structure was consolidated in vacuum at 140°C, which exceeds the melting temperature of CPE, for 15 minutes. The squeezed circles became a solid rod after consolidation process. Finally, inner core rod was inserted in PC tube and final structure of the preform was ready to draw. Figure 45 summarizes the whole preform fabrication processes. Unlike the other preform preparation processes, we did not perform final consolidation process, because during the fiber drawing we have already exceeded composite melting point, PC melted by holding the core material without any breaking.

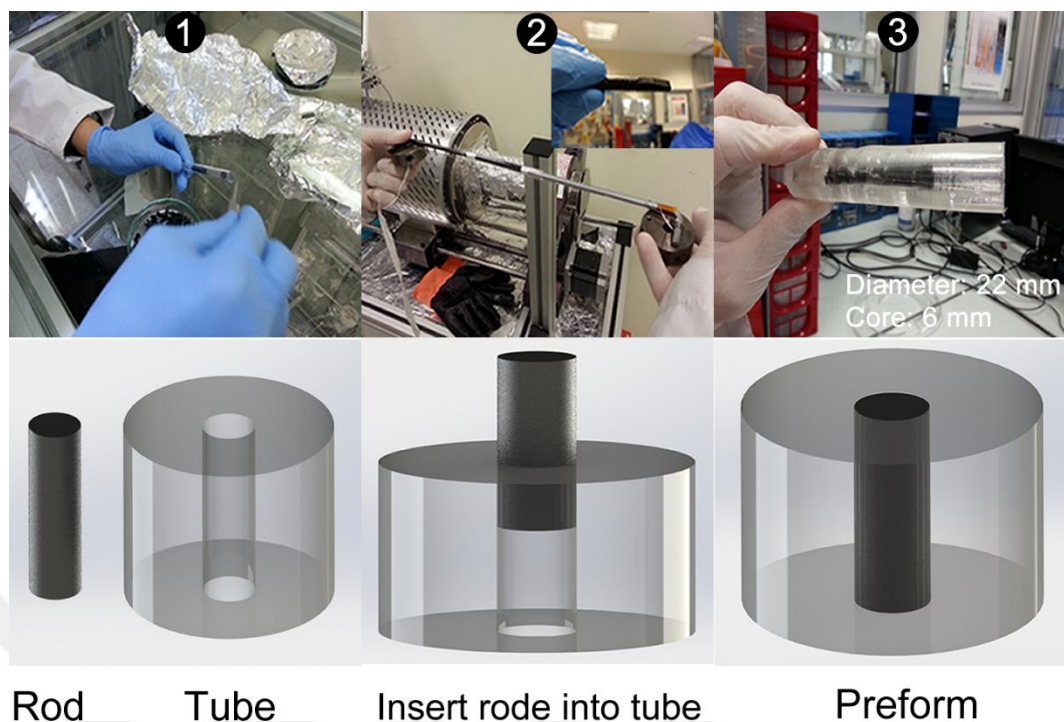


Figure 45. Schematic illustration of preform fabrication. The process starts with rod preparation (1, 2), final form of preform (3). PC cover preform was prepared and CPE/CNT composite rod was prepared by additional consolidation. Finally, composite rod was inserted into the PC tube.

4.5.2. Fiber Fabrication

Fiber drawing process was performed in a custom made fiber tower, which enables us to perform size reduction technique for multimaterial fibers in forms of micro and nanowires. Figure 46 summarizes the fabrication of kilometer long CPE/CNT composite micro and nanoribbon arrays, which includes several drawing steps. Initially, the process starts with breaking of macroscopic part from the preform, then adjusting temperature and tensile stress, the diameter of the core/cladding can be controlled. The drawing temperature was maintained as 240°C, results in a temperature in the core is higher than the melting temperature of the conductive polymer (10°C), the molten composite flows and shrinks in the PC cladding during the drawing process. The first step of the thermal drawing results in CPE/CNT microwires ranging between 300-800 μm in diameter. For the second step, 55 first step fibers were stacked and inserted into cylindrical hollow core of a new PC preform. As a result of one more fiber drawing procedure, diameters of 8-2 μm of composite wires were obtained.

Similarly, approximately 110 microwires were inserted again in a new PC preform, afterward thermal drawing was performed. After final drawing procedure, nanoribbons in thicknesses 300-50 nm were achieved.

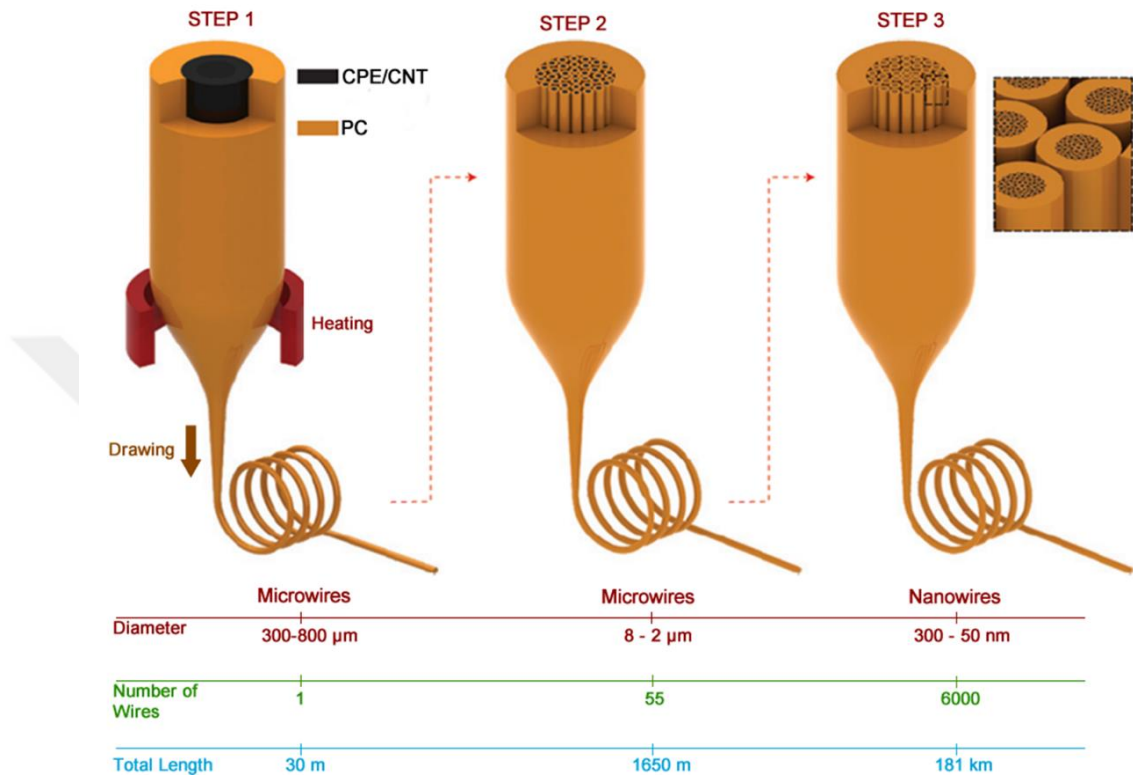


Figure 46. Fabrication schematic of micro and nanowires. Iterative size reduction technique scheme allows us to achieve multimaterial nanometer size structures. A macroscopic composite rod was inserted into a PC tube. Tens of meters long composite microribbons were encapsulated in PC. First step fibers were stacked and redrawn in a new PC preform in order to decrease size of the ribbons down to nanometers. Further size reduction can be achieved by following restacking and redrawing cycles.

4.5.3. Fiber Characterization

Morphological characterization of the micro and nanoribbons were performed by using SEM. Figure 47 represents the first step, second step and third step fibers. First column of the figure shows optical images of the tens of meters long multimaterial fibers and cross sectional image of 500 μm thick fiber. By etching PC cladding using dichloromethane (DCM), we can extract the composite fiber. Second column of the Figure 47 shows the SEM images of second step fibers, which are ranging from 8-2 μm thick. The carbon collapse from the surface of the fibers can be easily seen in the figure, this was occurred because of the highly thermal procedure was applied during the fiber drawing. However, this unexpected event did not cause any deformation on overall structure of the fibers. The third column represents the images of the third step fibers. Nanoribbons were again etched in DCM solution and dispersed onto a glass slide, SEM images confirmed that end of the third drawing process, we achieved fibers, which are in diameter of 300 - 100 nm.

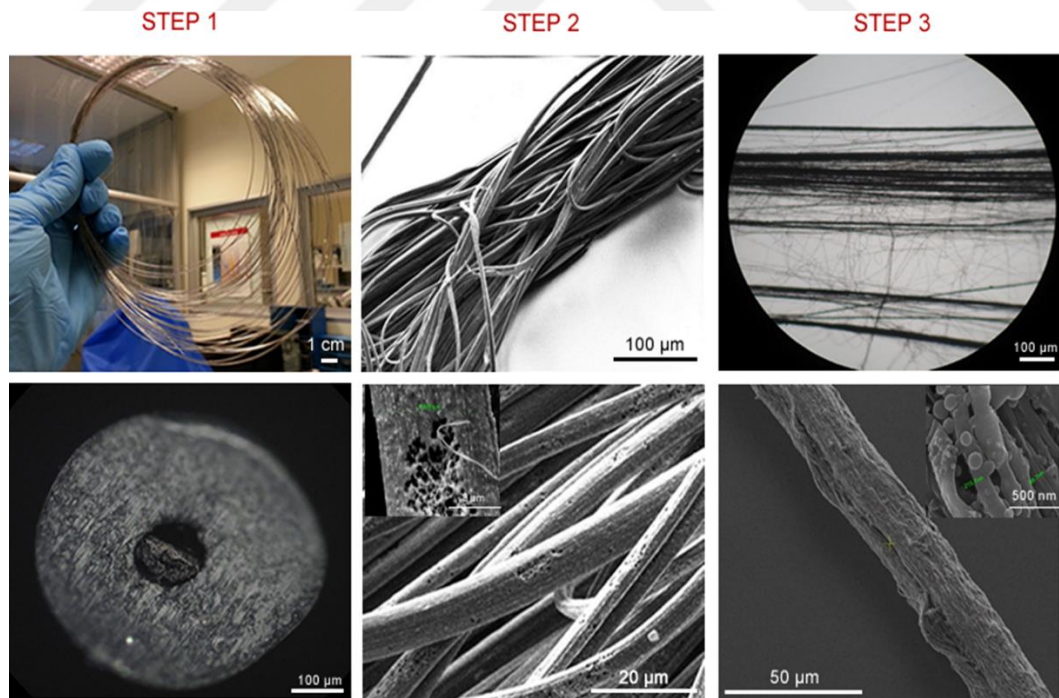


Figure 47. Optical and SEM images of micro and nanowires for each drawing step. CPE/CNT composite microribbon images obtained by etching the PC cladding. Cross sectional image

and macroscale image of first step fibers. SEM and optical images of both second step microwires and third step nanowires.

Alignment of CNT/CPE composite micro and nanofibers are investigated using SEM technique. As demonstrated in Figure 48, both second step and third step fibers are aligned in the drawing direction. The investigation of carbon nanotube alignment is rather difficult because of the differentiation of nanotubes from the polymer wires is very hard in case of using SEM images. Further investigations such as TEM, will be performed in order to observe carbon nanotube drawing.

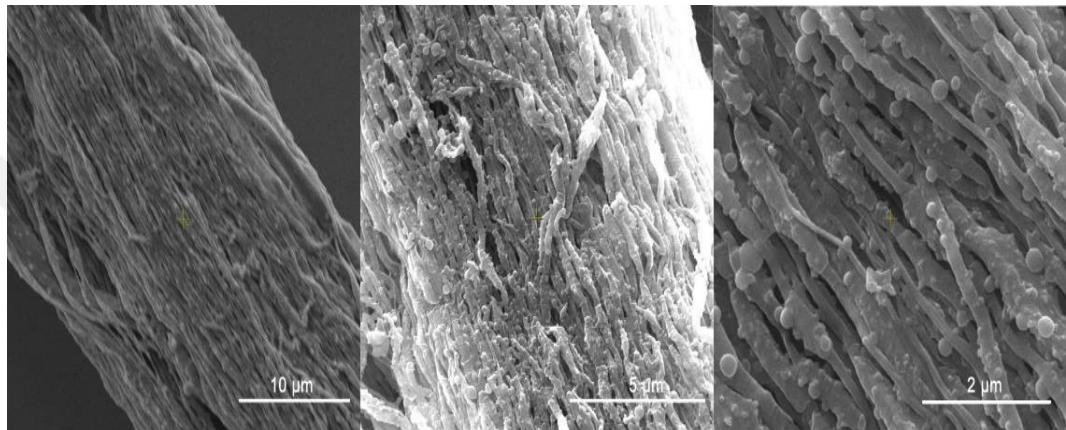


Figure 48. Alignment of micro and nanowires after applying iterative size reduction technique.

Chapter 5

Conclusions

5.1. Conclusions

In this work, inspired from human skin, we developed large area, transparent, flexible, passive matrix artificial skin with 100 pixels, able to sense very low pressure values, shear force, high and low frequency pressure stimulations. Next, we designed flexible, human skin compatible tiny device for monitoring electrocardiography signals. Cardiac measurements were performed directly from the various points of the human body that contains arterials such as neck, wrist, arm and chest. A model hand with 22 pressure sensors, which will be a candidate for developing prosthetics industry and human-like shape robotics, was demonstrated. The model hand is a replica of a human hand, which can sense touch, pressure actuations and perform human hand functions such as holding, grasping and hand-shaking. All devices were designed to demonstrate the function of the PVDF-TrFE nanoribbons for piezoelectric sensing and energy harvesting applications.

In order to improve the piezoelectric coefficient of the previous work's materials, we fabricated a highly crystalline, uniform PVDF-TrFE by melt-pressing technique and we applied thermal fiber drawing to have highly crystalline, high piezoelectric coefficient, microwires that represent piezoelectric β phase dominantly in the form of fiber. Phase transition mechanism was explained from the bulk nonpolar α phase to ferroelectric β phase by comparing bulk film, drawn fibers and thermally annealed fibers that were cured between the Curie and melting temperature. Tens of meters long first step fibers were fabricated between 80 μm to 450 μm diameter. Additionally, one size reduction was applied to first step fibers in order to have several micron and sub-micron thick PVDF-TrFE fibers.

Our next target was to develop polymer based, highly conductive, flexible nanocomposites, which are promising candidates for electrode applications in flexible electronics. To do that, we fabricated a conductive CPE /CNT nanocomposite film that achieves a uniform conductivity of $\sim 10^3$ S/m with various thicknesses. Further, by processing nanocomposite conductive films, we fabricated a bulk rod and processed it through three steps of size reduction technique, which allowed us to have composed fibers whose diameters range from 100 μm to 100 nm.



Bibliography

- [1] J. A. Rogers, T. Someya, and Y. Huang, “Materials and mechanics for stretchable electronics.” *Science*, vol. 327, no. 2010, pp. 1603–1607, 2010.
- [2] T. Sekitani, U. Zschieschang, H. Klauk, and T. Someya, “Flexible organic transistors and circuits with extreme bending stability.” *Nat. Mater.*, vol. 9, no. 12, pp. 1015–1022, 2010.
- [3] A. Nathan, A. Ahnood, M. T. Cole, S. Lee, Y. Suzuki, P. Hiralal, F. Bonaccorso, T. Hasan, L. Garcia-Gancedo, A. Dyadyusha, S. Haque, P. Andrew, S. Hofmann, J. Moultrie, D. Chu, A. J. Flewitt, A. C. Ferrari, M. J. Kelly, J. Robertson, G. A. J. Amaratunga, and W. I. Milne, “Flexible electronics: The next ubiquitous platform,” *Proc. IEEE*, vol. 100, no. SPL CONTENT, pp. 1486–1517, 2012.
- [4] D.-H. Kim, J.-H. Ahn, W.M. Choi, S.-S.Lim, T.-H. Kim, J. Song, Y.Y. Huang, Z. Liu, C.Lu and J. A. Rogers, “Stretchable and Foldable Silicon Integrated Electronics,” *Science (80-.)*, vol. 320, no. 5875, pp. 507–511, 2008.
- [5] D.-Y. Khang, H. Jiang, Y. Huang, and J. A. Rogers, “A Stretchable Form of Single-Crystal Silicon for high performance electronics on rubber substrates,” *Science (80-.)*, vol. 311, no. January, pp. 208–212, 2006.
- [6] Y. Sun and J. A. Rogers, “Inorganic semiconductors for flexible electronics,” *Adv. Mater.*, vol. 19, no. 15, pp. 1897–1916, 2007.
- [7] T. Sekitani, M. Takamiya, Y. Noguchi, S. Nakano, Y. Kato, T. Sakurai, and T. Someya, “A large-area wireless power-transmission sheet using printed organic transistors and plastic MEMS switches,” *Nat. Mater.*, vol. 6, no. 6, pp. 413–7, Jun. 2007.
- [8] J. Yoon, A. J. Baca, S.-I. Park, P. Elvikis, J. B. Geddes, L. Li, R. H. Kim, J. Xiao, S. Wang, T.-H. Kim, M. J. Motala, B. Y. Ahn, E. B. Duoss, J. a Lewis, R. G. Nuzzo, P. M. Ferreira, Y. Huang, A. Rockett, and J. a Rogers, “Ultrathin

- silicon solar microcells for semitransparent, mechanically flexible and microconcentrator module designs.,” *Nat. Mater.*, vol. 7, no. 11, pp. 907–915, 2008.
- [9] M. Kaltenbrunner, M. S. White, E. D. Głowacki, T. Sekitani, T. Someya, N. S. Sariciftci, and S. Bauer, “Ultrathin and lightweight organic solar cells with high flexibility,” *Nat. Commun.*, vol. 3, p. 770, 2012.
- [10] I. Jung, J. Xiao, V. Malyarchuk, C. Lu, M. Li, Z. Liu, J. Yoon, Y. Huang, and J. A. Rogers, “Dynamically tunable hemispherical electronic eye camera system with adjustable zoom capability.,” *Proc. Natl. Acad. Sci. U. S. A.*, vol. 108, no. 5, pp. 1788–93, 2011.
- [11] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, and T. Someya, “Stretchable active-matrix organic light-emitting diode display using printable elastic conductors.,” *Nat. Mater.*, vol. 8, no. 6, pp. 494–499, Jun. 2009.
- [12] T. Yokota, P. Zalar, M. Kaltenbrunner, H. Jinno, N. Matsuhisa, H. Kitanosako, Y. Tachibana, W. Yukita, M. Koizumi, and T. Someya, “Ultra-flexible Organic Photonic Skin,” *Sci. Adv.*, no. April, pp. 1–9, 2016.
- [13] M. L. Hammock, A. Chortos, B. C.-K. Tee, J. B.-H. Tok, and Z. Bao, “25th anniversary article: The evolution of electronic skin (e-skin): a brief history, design considerations, and recent progress.” *Adv. Mater.*, vol. 25, no. 42, pp. 5997–6038, Nov. 2013.
- [14] T. Someya, T. Sekitani, S. Iba, Y. Kato, H. Kawaguchi, and T. Sakurai, “A large-area, flexible pressure sensor matrix with organic field-effect transistors for artificial skin applications.,” *Proc. Natl. Acad. Sci. U. S. A.*, vol. 101, no. 27, pp. 9966–70, Jul. 2004.
- [15] Y. Yang, H. Zhang, Z. H. Lin, Y. S. Zhou, Q. Jing, Y. Su, J. Yang, J. Chen, C. Hu, and Z. L. Wang, “Human skin based triboelectric nanogenerators for harvesting biomechanical energy and as self-powered active tactile sensor system,” *ACS Nano*, vol. 7, no. 10, pp. 9213–9222, 2013.

- [16] M. Kaltenbrunner, T. Sekitani, J. Reeder, T. Yokota, K. Kuribara, T. Tokuhara, M. Drack, R. Schwödiauer, I. Graz, S. Bauer-Gogonea, S. Bauer, and T. Someya, “An ultra-lightweight design for imperceptible plastic electronics.,” *Nature*, vol. 499, no. 7459, pp. 458–63, 2013.
- [17] H. Athenstaedt, H. Claussen, and D. Schaper, “Epidermis of human skin: pyroelectric and piezoelectric sensor layer,” *Science*, vol. 216, no. 4549, pp. 1018–1020, 1982.
- [18] J. A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, V. R. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing, and P. Drzaic, “Paper-like electronic displays: large-area rubber-stamped plastic sheets of electronics and microencapsulated electrophoretic inks.,” *Proc. Natl. Acad. Sci. U. S. A.*, vol. 98, no. 9, pp. 4835–40, 2001.
- [19] K. Takei, T. Takahashi, J. C. Ho, H. Ko, A. G. Gillies, P. W. Leu, R. S. Fearing, and A. Javey, “Nanowire active-matrix circuitry for low-voltage macroscale artificial skin.,” *Nat. Mater.*, vol. 9, no. 10, pp. 821–6, 2010.
- [20] T. Takahashi, K. Takei, A. G. Gillies, R. S. Fearing, and A. Javey, “Carbon nanotube active-matrix backplanes for conformal electronics and sensors.,” *Nano Lett.*, pp. 5408–5413, 2011.
- [21] L. Pan, A. Chortos, G. Yu, Y. Wang, S. Isaacson, R. Allen, Y. Shi, R. Dauskardt, and Z. Bao, “An ultra-sensitive resistive pressure sensor based on hollow-sphere microstructure induced elasticity in conducting polymer film,” *Nat. Commun.*, vol. 5, p. 3002, 2014..
- [22] A. Yildirim, M. Vural, M. Yaman, and M. Bayindir, “Bioinspired optoelectronic nose with nanostructured wavelength-scalable hollow-core infrared fibers,” *Adv. Mater.*, vol. 23, no. 10, pp. 1263–1267, 2011.
- [23] M. Yaman, T. Khudiyev, E. Ozgur, M. Kanik, O. Aktas, E. O. Ozgur, H. Deniz, E. Korkut, and M. Bayindir, “Arrays of indefinitely long uniform nanowires and nanotubes.,” *Nat. Mater.*, vol. 10, no. 7, pp. 494–501, 2011.

- [24] S. Egusa, Z. Wang, N. Chocat, Z. M. Ruff, a M. Stolyarov, D. Shemuly, F. Sorin, P. T. Rakich, J. D. Joannopoulos, and Y. Fink, “Multimaterial piezoelectric fibres,” *Nat. Mater.*, vol. 9, no. 8, pp. 643–648, 2010.
- [25] M. Kanik, O. Aktas, H. S. Sen, E. Durgun, M. Bayindir, and M. Science, “Spontaneous High Piezoelectricity in Poly(vinylidene fluoride) Nanoribbons,” *ACS Nano*, vol. 8, no. 9, pp. 9311–9323, 2014.
- [26] Y. Qi and M. C. McAlpine, “Nanotechnology-enabled flexible and biocompatible energy harvesting,” *Energy Environ. Sci.*, vol. 3, no. 9, p. 1275, 2010.
- [27] M. Kanik, M. G. Say, B. Daglar, A. F. Yavuz, M. H. Dolas, M. M. El-Ashry, and M. Bayindir, “A motion- and sound-activated, 3d-printed, chalcogenide-based triboelectric nanogenerator,” *Adv. Mater.*, vol. 27, no. 14, pp. 2367–2376, 2015
- [28] G. M. Spinks, V. Mottaghitalab, M. Bahrami-Samani, P. G. Whitten, and G. G. Wallace, “Carbon-nanotube-reinforced polyaniline fibers for high-strength artificial muscles,” *Adv. Mater.*, vol. 18, no. 5, pp. 637–640, 2006.
- [29] J. X. Zhang, B. Xiang, Q. He, J. Seidel, R. J. Zeches, P. Yu, S. Y. Yang, C. H. Wang, Y.-H. Chu, L. W. Martin, a M. Minor, and R. Ramesh, “Large field-induced strains in a lead-free piezoelectric material,” *Nat. Nanotechnol.*, vol. 6, no. 2, pp. 98–102, 2011.
- [30] V. Cauda, G. Canavese, and S. Stassi, “Nanostructured piezoelectric polymers,” *J. Appl. Polym. Sci.*, vol. 132, no. 13, pp. 1–14, 2015.
- [31] A. Kholkin, N. Amdursky, I. Bdikin, E. Gazit, and G. Rosenman, “Strong piezoelectricity in bioinspired peptide nanotubes,” *ACS Nano*, vol. 4, no. 2, pp. 610–614, 2010.
- [32] M. D. Ward and D. A. Buttry, “In Situ Interfacial Mass Detection with Piezoelectric Transducers,” *Science*, vol. 249, no. 4972, pp. 1000–1007, 1990.

- [33] C. Masmanidis, R. B. Karabalin, I. De Vlaminck, G. Borghs, M. R. Freeman, and M. L. Roukes, “Multifunctional nanomechanical systems via tunably coupled piezoelectric actuation.,” *Science*, vol. 317, no. 5839, pp. 780–3, 2007..
- [34] K.Y. Ma, P. Chiraratananon, S.B. Fuller, R.J. Wood, “Controlled flight of a biologically inspired, insect-scale robot”, *Science*, vol.340, no.6132, pp. 603–608, 2013.
- [35] Z. L. Wang and J. Song, “Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays,” *Science*, vol. 312, no. 5771, pp. 242–246, 2006.
- [36] T. D. Nguyen, N. Deshmukh, J. M. Nagarah, T. Kramer, P. K. Purohit, M. J. Berry, and M. C. McAlpine, “Piezoelectric nanoribbons for monitoring cellular deformations,” *Nat Nanotechnol*, vol. 7, no. 9, pp. 587–593, 2012.
- [37] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, “Lead-free piezoceramics,” *Nature*, vol. 432, no.7013, pp. 84-87, 2004.
- [38] H. KAWAJ, “The piezoelectricity of poly (vinylidene fluoride),” *J Appl. Phys.*, vol. 8, p. 975, 1969.
- [39] V. Cauda, B. Torre, A. Falqui, G. Canavese, S. Stassi, T. Bein, and M. Pizzi, “Confinement in oriented mesopores induces piezoelectric behavior of polymeric nanowires,” *Chem. Mater.*, vol. 24, no. 21, pp. 4215–4221, 2012.
- [40] A. Aliane, M. Benwadih, B. Bouthinon, R. Coppard, F. Domingues-Dos Santos, and A. Daami, “Impact of crystallization on ferro-, piezo- and pyro-electric characteristics in thin film P(VDF–TrFE),” *Org. Electron.*, vol. 25, pp. 92–98, 2015.
- [41] A.H.Meitzler, H.F.Tiersten, “An American National Standard IEEE Standard on Piezoelectricity,” 1987
- [42] Piezoelectric Ceramics: Principles and Applications, APC International, Ltd., 2011.

- [43] S. B. Lang and S. Muensit, "Review of some lesser-known applications of piezoelectric and pyroelectric polymers," *Appl. Phys. A Mater. Sci. Process.*, vol. 85, no. 2, pp. 125–134, 2006.
- [44] S. R. Anton and H. A. Sodano, "A review of power harvesting using piezoelectric materials (2003-2006)," *Smart Mater. Struct.*, vol. 16, no. 3, pp. R1–R21, 2007.
- [45] *Fundamentals of Piezoelectric Sensorics*, Springer, 2010.
- [46] *Piezoelectric Nanomaterials for Biomedical Applications*, Springer, 2011.
- [47] S. Iijima, "Helical Microtubules of Graphitic Carbon," *Nature*, vol. 354, pp. 56–58, Nov 7 1991.
- [48] H.-S.P. Wong, D. Akinwande, *Carbon Nanotube and Graphene Device Physics*, Cambridge, 2011.
- [49] M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, *Carbon nanotubes: synthesis, structure, properties, and applications*. Berlin; New York: Springer, 2001.
- [50] E. A. Laird, F. Kuemmeth, G. Steele, K. Grove-Rasmussen, J. N. Rd, K. Flensberg, and L. P. Kouwenhoven, "Quantum transport in carbon nanotubes," *Rev. Mod. Phys.*, vol. 87, p. 703, 2015.
- [51] A. Javey, J. Kong, 'Carbon Nanotube Electronics', Springer, New York, 2009.
- [52] A. Nathan, A. Ahnood, M. T. Cole, S. Lee, Y. Suzuki, P. Hiralal, F. Bonaccorso, T. Hasan, L. Garcia-Gancedo, A. Dyadyusha, S. Haque, P. Andrew, S. Hofmann, J. Moultrie, D. Chu, A. J. Flewitt, A. C. Ferrari, M. J. Kelly, J. Robertson, G. A. J. Amaratunga, and W. I. Milne, "Flexible electronics: The next ubiquitous platform," *Proc. IEEE*, vol. 100, no. SPL CONTENT, pp. 1486–1517, 2012.
- [53] L. Persano, C. Dagdeviren, Y. Su, Y. Zhang, S. Girardo, D. Pisignano, Y. Huang, and J. a Rogers, "High performance piezoelectric devices based on

aligned arrays of nanofibers of poly(vinylidene fluoride-co-trifluoroethylene).,” *Nat. Commun.*, vol. 4, p. 1633, 2013.

- [54] B. Chu, X. Zhou, K. Ren, B. Neese, M. Lin, Q. Wang, F. Bauer, and Q. M. Zhang, “A Dielectric Polymer with High Electric Energy Density and Fast Discharge Speed,” *Science (80-.)*, vol. 313, no. 5785, pp. 334–336, 2006.
- [55] C. C. Hong, S. Y. Huang, J. Shieh, and S. H. Chen, “Enhanced piezoelectricity of nanoimprinted sub-20 nm poly (vinylidene fluoride-trifluoroethylene) copolymer nanograss,” *Macromolecules*, vol. 45, no. 3, pp. 1580–1586, 2012.
- [56] C. Chang, V. H. Tran, J. Wang, Y. K. Fuh, and L. Lin, “Direct-write piezoelectric polymeric nanogenerator with high energy conversion efficiency,” *Nano Lett.*, vol. 10, no. 2, pp. 726–731, 2010.
- [57] Neuroscience, 2nd Edition, Sinauer Associates, 2001.
- [58] J. Dargahi and S. Najarian, “Human tactile perception as a standard for artificial tactile sensing - a review.” *Int. J. Med. Robot.*, vol. 1, no. 1, pp. 23–35, 2004.
- [59] H.-H. Chou, A. Nguyen, A. Chortos, J. W. F. To, C. Lu, J. Mei, T. Kurosawa, W.-G. Bae, J. B.-H. Tok, and Z. Bao, “A chameleon-inspired stretchable electronic skin with interactive colour changing controlled by tactile sensing.” *Nat. Commun.*, vol. 6, p. 8011, 2015.
- [60] S. Gong, W. Schwalb, Y. Wang, Y. Chen, Y. Tang, J. Si, B. Shirinzadeh, and W. Cheng, “A wearable and highly sensitive pressure sensor with ultrathin gold nanowires,” *Nat. Commun.*, vol. 5, p. 3132, 2014.
- [61] J. Park, M. Kim, Y. Lee, H. S. Lee, and H. Ko, “Fingertip skin-inspired microstructured ferroelectric skins discriminate static/dynamic pressure and temperature stimuli,” *Sci. Adv.*, vol. 1, no. 9, pp. e1500661–e1500661, 2015.
- [62] D. J. Lipomi, M. Vosgueritchian, B. C.-K. Tee, S. L. Hellstrom, J. a Lee, C. H. Fox, and Z. Bao, “Skin-like pressure and strain sensors based on transparent elastic films of carbon nanotubes.” *Nat. Nanotechnol.*, vol. 6, no. 12, pp. 788–

92, Dec. 2011.

- [63] C. Metzger, E. Fleisch, J. Meyer, M. Dansachmuller, I. Graz, M. Kaltenbrunner, C. Keplinger, R. Schweudiauer, and S. Bauer, "Flexible-foam-based capacitive sensor arrays for object detection at low cost," *Appl. Phys. Lett.*, vol. 92, no. 1, pp. 1–4, 2008.
- [64] C. Dagdeviren, Y. Su, P. Joe, R. Yona, Y. Liu, Y.-S. Kim, Y. Y. Huang, A. R. Damadoran, J. Xia, L. W. Martin, and J. a Rogers, "Conformable amplified lead zirconate titanate sensors with enhanced piezoelectric response for cutaneous pressure monitoring.," *Nat. Commun.*, vol. 5, p. 4496, 2014.
- [65] Y. Qi, N. T. Jafferis, K. Lyons, C. M. Lee, H. Ahmad, and M. C. McAlpine, "Piezoelectric ribbons printed onto rubber for flexible energy conversion," *Nano Lett.*, vol. 10, no. 2, pp. 524–525, 2010.
- [66] T. Sekitani, T. Yokota, U. Zschieschang, H. Klauk, S. Bauer, K. Takeuchi, M. Takamiya, T. Sakurai, and T. Someya, "Transistors for Flexible Sensor Arrays," *Science (80-.)*, vol. 326, pp. 1516–1519, 2009..
- [67] C. Dagdeviren, B. D. Yang, Y. Su, P. L. Tran, P. Joe, E. Anderson, J. Xia, V. Doraiswamy, B. Dehdashti, X. Feng, B. Lu, R. Poston, Z. Khalpey, R. Ghaffari, Y. Huang, M. J. Slepian, and J. A. Rogers, "Conformal piezoelectric energy harvesting and storage from motions of the heart, lung, and diaphragm.," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 111, no. 5, pp. 1927–32, 2014.
- [68] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D. N. Futaba, and K. Hata, "A stretchable carbon nanotube strain sensor for human-motion detection.," *Nat. Nanotechnol.*, vol. 6, no. 5, pp. 296–301, 2011.
- [69] C. Yan, J. Wang, W. Kang, M. Cui, X. Wang, C. Y. Foo, K. J. Chee, and P. S. Lee, "Highly stretchable piezoresistive graphene-nanocellulose nanopaper for strain sensors," *Adv. Mater.*, vol. 26, no. 13, pp. 2022–2027, 2014.
- [70] B.C.-K. Tee and A.Chortos, and A.Berndt, A.K. Nguyen, A.Tom, A.McGuire,Z.C. Lin, K.Tien, W.-G.Bae, H. Wang, P.Mei, H.-H. Chou, B.Cuim

- K. Deisseroth, T.N.Ng, Z. Bao, “A skin inspired organic digital mechanoreceptor,” *Science*, pp. 350, 313–316, 2015.
- [71] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, and H. Yan, “One-Dimensional Nanostructures: Synthesis, Characterization, and Applications,” *Adv. Mater.*, vol. 15, no. 5, pp. 353–389, 2003.
- [72] V. Cauda, S. Stassi, K. Bejtka, and G. Canavese, “Nanoconfinement: An effective way to enhance PVDF piezoelectric properties,” *ACS Appl. Mater. Interfaces*, vol. 5, no. 13, pp. 6430–6437, 2013.
- [73] S. J. Kang, I. Bae, Y. J. Shin, Y. J. Park, J. Huh, S. M. Park, H. C. Kim, and C. Park, “Nonvolatile polymer memory with nanoconfinement of ferroelectric crystals,” *Nano Lett.*, vol. 11, no. 1, pp. 138–144, 2011.
- [74] Y. Wu, Q. Gu, G. Ding, F. Tong, Z. Hu, and A. M. Jonas, “Confinement induced preferential orientation of crystals and enhancement of properties in ferroelectric polymer nanowires,” *ACS Macro Lett.*, vol. 2, no. 6, pp. 535–538, 2013.
- [75] X. Li, Y.-F. Lim, K. Yao, F. E. H. Tay, and K. H. Seah, “P(VDF-TrFE) ferroelectric nanotube array for high energy density capacitor applications,” *Phys. Chem. Chem. Phys.*, vol. 15, no. 2, pp. 515–20, 2013.
- [76] C. C. Wang, Q. D. Shen, S. C. Tang, Q. Wu, H. M. Bao, C. Z. Yang, and X. Q. Jiang, “Ferroelectric polymer nanotubes with large dielectric constants for potential all-organic electronic devices,” *Macromol. Rapid Commun.*, vol. 29, no. 9, pp. 724–728, 2008.
- [77] S. Oh, Y. Kim, Y. Y. Choi, D. Kim, H. Choi, and K. No, “Fabrication of vertically well-aligned P (VDF-TrFE) nanorod arrays,” *Adv. Mater.*, vol. 24, no. 42, pp. 5708–5712, 2012.
- [78] Z. Hu, M. Tian, B. Nysten, and A. M. Jonas, “Regular arrays of highly ordered ferroelectric polymer nanostructures for non-volatile low-voltage memories,” *Nat. Mater.*, vol. 8, no. 1, pp. 62–67, 2009.

- [79] Y. J. Park, S. J. Kang, Y. Shin, R. H. Kim, I. Bae, and C. Park, “Non-volatile memory characteristics of epitaxially grown PVDF-TrFE thin films and their printed micropattern application,” *Curr. Appl. Phys.*, vol. 11, no. 2 SUPPL., pp. e30–e34, 2011.
- [80] Y. Liu, D. N. Weiss, and J. Li, “Rapid nanoimprinting and excellent piezoresponse of polymeric ferroelectric nanostructures,” *ACS Nano*, vol. 4, no. 1, pp. 83–90, 2010.
- [81] X. Z. Chen, Q. Li, X. Chen, X. Guo, H. X. Ge, Y. Liu, and Q. D. Shen, “Nano-imprinted ferroelectric polymer nanodot arrays for high density data storage,” *Adv. Funct. Mater.*, vol. 23, no. 24, pp. 3124–3129, 2013.
- [82] H. G. Kassa, R. Cai, A. Marrani, B. Nysten, Z. Hu, and A. M. Jonas, “Structure and ferroelectric properties of nanoimprinted poly(vinylidene fluoride-ran-trifluoroethylene),” *Macromolecules*, vol. 46, no. 21, pp. 8569–8579, 2013.
- [83] J. Y. Son, I. Jung, and Y. H. Shin, “Formation of locally crystallized ferroelectric Poly(vinylidene fluoride- ran -trifluoroethylene) nanodots based on heated atomic force microscopy,” *J. Phys. Chem. C*, vol. 117, no. 24, pp. 12890–12894, 2013.
- [84] J. Song, H. Lu, S. Li, L. Tan, A. Gruverman, and S. Ducharme, “Fabrication of ferroelectric polymer nanostructures on flexible substrates by soft-mold reverse nanoimprint lithography,” *Nanotechnology*, vol. 27, no. 1, p. 015302, 2016.
- [85] N. Weber, Y. S. Lee, S. Shanmugasundaram, M. Jaffe, and T. L. Arinze, “Characterization and in vitro cytocompatibility of piezoelectric electrospun scaffolds,” *Acta Biomater.*, vol. 6, no. 9, pp. 3550–3556, 2010.
- [86] Y. S. Lee, G. Collins, and T. Livingston Arinze, “Neurite extension of primary neurons on electrospun piezoelectric scaffolds,” *Acta Biomater.*, vol. 7, no. 11, pp. 3877–3886, 2011.
- [87] Lovinger, A.F., *Science*, 220, 1115, 1983.

- [88] D. Mandal, S. Yoon, and K. J. Kim, "Origin of piezoelectricity in an electrospun poly (vinylidene fluoride-trifluoroethylene) nanofiber web-based nanogenerator and nano-pressure sensor," *Macromol. Rapid Commun.*, vol. 32, no. 11, pp. 831–837, 2011.
- [89] A. Gruverman and S. V. Kalinin, "Piezoresponse force microscopy and recent advances in nanoscale studies of ferroelectrics," *Front. Ferroelectr. A Spec. Issue J. Mater. Sci.*, vol. 1, no. 1, pp. 107–116, 2007.
- [90] M. Baniasadi, Z. Xu, S. Hong, M. Naraghi, and M. Minary-Jolandan, "Thermo-electromechanical Behavior of Piezoelectric Nanofibers," *ACS Appl. Mater. Interfaces*, p. acsami.5b10073, 2016.
- [91] R. I. Mahdi, W. C. Gan, and W. H. Abd Majid, "Hot plate annealing at a low temperature of a thin ferroelectric P(VDF-TrFE) film with an improved crystalline structure for sensors and actuators," *Sensors (Switzerland)*, vol. 14, no. 10, pp. 19115–19127, 2014.
- [92] H. Kodama, Y. Takahashi, and T. Furukawa, "Effects of annealing on the structure and switching characteristics of VDF/TrFE copolymers," *Ferroelectrics*, vol. 203, no. 1, pp. 433–455, 1997.
- [93] G. Teyssedre, "DSC and TSC study of a VDF / TrFE copolymer '," vol. 226, no. September 1992, pp. 65–75, 1993.
- [94] K. Lau, Y. Liu, H. Chen, and R. Withers, "Effect of Annealing Temperature on the Morphology and Piezoresponse Characterisation of Poly (vinylidene fluoride-trifluoroethylene) Films via Scanning Probe," *Adv. Condens. Matter ...*, vol. 2013, 2013.
- [95] Sekitani, T., Noguchi, Y., Hata, K., Fukushima, T., Aida, T., and Someya, T. (2008). A rubberlike Stretchable Active Matrix Using Elastic Conductors. *Science (New York, NY)*, (September), 1895–1900.
- [96] Li, Z., Zhang, R., Moon, K. S., Liu, Y., Hansen, K., Le, T., and Wong, C. P. (2013). Highly conductive, flexible, polyurethane-based adhesives for flexible

- and printed electronics. *Advanced Functional Materials*, 23(11), 1459–1465. doi:10.1002/adfm.201202249.
- [97] Jung, H. C., Moon, J. H., Baek, D. H., Lee, J. H., Choi, Y. Y., Hong, J. S., and Lee, S. H. (2012). CNT/PDMS composite flexible dry electrodes for long-term ECG monitoring. *IEEE Transactions on Biomedical Engineering*, 59(5), 1472–1479. doi:10.1109/TBME.2012.2190288.
- [98] Meng, C., Liu, C., Chen, L., Hu, C., and Fan, S. (2010). Highly flexible and all-solid-state paperlike polymer supercapacitors. *Nano Letters*, 10(10), 4025–4031. doi:10.1021/nl1019672.
- [99] Yao, S., and Zhu, Y. (2015). Nanomaterial-enabled stretchable conductors: Strategies, materials and devices. *Advanced Materials*, 27(9), 1480–1511. doi:10.1002/adma.201404446.
- [100] Xu, F., and Zhu, Y. (2012). Highly conductive and stretchable silver nanowire conductors. *Advanced Materials (Deerfield Beach, Fla.)*, 24(37), 5117–22. doi:10.1002/adma.201201886.
- [101] Park, M., Im, J., Shin, M., Min, Y., Park, J., Cho, Kim, K. (2012). Highly stretchable electric circuits from a composite material of silver nanoparticles and elastomeric fibres. *Nature Nanotechnology*, 7(12), 803–9. doi:10.1038/nnano.2012.206.
- [102] Hu, W., Niu, X., Li, L., Yun, S., Yu, Z., and Pei, Q. (2012). Intrinsically stretchable transparent electrodes based on silver-nanowire-crosslinked-polyacrylate composites. *Nanotechnology*, 23(34), 344002. doi:10.1088/0957-4484/23/34/344002.
- [103] Chen, M., Zhang, L., Duan, S., Jing, S., Jiang, H., and Li, C. (2014). Highly stretchable conductors integrated with a conductive carbon nanotube/graphene network and 3D porous poly (dimethylsiloxane). *Advanced Functional Materials*, 24(47), 7548–7556. doi:10.1002/adfm.201401886.
- [104] Li, Z., Zhang, R., Moon, K. S., Liu, Y., Hansen, K., Le, T., and Wong, C. P.

- (2013). Highly conductive, flexible, polyurethane-based adhesives for flexible and printed electronics. *Advanced Functional Materials*, 23(11), 1459–1465. doi:10.1002/adfm.201202249.
- [105] Seyedin, M. Z., Razal, J. M., Innis, P. C., and Wallace, G. G. (2014). Strain-responsive polyurethane/PEDOT: PSS elastomeric composite fibers with high electrical conductivity. *Advanced Functional Materials*, 24(20), 2957–2966. doi:10.1002/adfm.201303905.
- [106] Kim, K. H., Vural, M., and Islam, M. F. (2011). Single-walled carbon nanotube aerogel-based elastic conductors. *Advanced Materials (Deerfield Beach, Fla.)*, 23(25), 2865–9. doi:10.1002/adma.201100310.
- [107] Kim, T. A., Kim, H. S., Lee, S. S., and Park, M. (2012). Single-walled carbon nanotube/silicone rubber composites for compliant electrodes. *Carbon*, 50(2), 444–449. doi:10.1016/j.carbon.2011.08.070.
- [108] Park, M., Park, J., and Jeong, U. (2014). Design of conductive composite elastomers for stretchable electronics. *Nano Today*, 9(2), 244–260. doi:10.1016/j.nantod.2014.04.009.
- [109] Wagner, S., and Bauer, S. (2012). Materials for stretchable electronics. *MRS Bulletin*, 37(03), 207–213. doi:10.1557/mrs.2012.37.
- [110] W. Zhang, A. a. Dehghani-Sanij, and R. S. Blackburn, “Carbon based conductive polymer composites,” *J. Mater. Sci.*, vol. 42, no. 10, pp. 3408–3418, Mar. 2007.
- [111] S. Rosset and H. R. Shea, “Flexible and stretchable electrodes for dielectric elastomer actuators,” *Appl. Phys. A*, vol. 110, no. 2, pp. 281–307, Nov. 2012.
- [112] M. T. Byrne and Y. K. Gun’ko, “Recent Advances in Research on Carbon Nanotube-Polymer Composites,” *Adv. Mater.*, vol. 22, no. 15, pp. 1672–1688, 2010.
- [113] Z. Spitalsky, D. Tasis, K. Papagelis, and C. Galiotis, “Carbon nanotube–

- polymer composites: Chemistry, processing, mechanical and electrical properties,” *Prog. Polym. Sci.*, vol. 35, no. 3, pp. 357–401, Mar. 2010.
- [114] Y. Y. Huang and E. M. Terentjev, “Tailoring the Electrical Properties of Carbon Nanotube-Polymer Composites,” *Adv. Funct. Mater.*, vol. 20, no. 23, pp. 4062–4068, Dec. 2010.
- [115] K. Liu, Y. Sun, P. Liu, X. Lin, S. Fan, and K. Jiang, “Cross-Stacked Superaligned Carbon Nanotube Films for Transparent and Stretchable Conductors,” *Adv. Funct. Mater.*, vol. 21, no. 14, pp. 2721–2728, Jul. 2011.
- [116] P. Pötschke, A. R. Bhattacharyya, and A. Janke, “Carbon nanotube-filled polycarbonate composites produced by melt mixing and their use in blends with polyethylene,” *Carbon N. Y.*, vol. 42, no. 5–6, pp. 965–969, 2004
- [117] J. Wang, J. Dai, and T. Yarlagadda, “Carbon nanotube-conducting-polymer composite nanowires,” *Langmuir*, vol. 21, no. 1, pp. 9–12, 2005
- [118] N. Ferrer-Anglada, M. Kaempgen, V. Skákalová, U. Dettlaf-Weglikowska, and S. Roth, “Synthesis and characterization of carbon nanotube-conducting polymer thin films,” *Diam. Relat. Mater.*, vol. 13, no. 2, pp. 256–260, 2004
- [119] M. K. Shin, J. Oh, M. Lima, M. E. Kozlov, S. J. Kim, and R. H. Baughman, “Elastomeric conductive composites based on carbon nanotube forests,” *Adv. Mater.*, vol. 22, no. 24, pp. 2663–7, Jun. 2010
- [120] L. Bokobza and J. Zhang, “Raman spectroscopic characterization of multiwall carbon nanotubes and of composites,” *Express Polym. Lett.*, vol. 6, no. 7, pp. 601–608, 2012.