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MASTER'S THESIS

Brno 2021 Bc. Denis Misiurev

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FACULTY OF ELECTRICAL ENGINEERING AND COMMUNICATION
FAKULTA ELEKTROTECHNIKY A KOMUNIKAČNÍCH TECHNOLOGIÍ

DEPARTMENT OF MICROELECTRONICS
ÚSTAV MIKROELEKTRONIKY

STRUCTURAL AND ELECTRICAL PROPERTIES OF PVDF-CNT COMPOSITE

STRUKTURÁLNÍ A ELEKTRICKÉ VLASTNOSTI PVDF-CNT KOMPOZITU

MASTER'S THESIS
DIPLOMOVÁ PRÁCE

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VEDOUCÍ PRÁCE

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BRNO UNIVERSITY OF TECHNOLOGY
FACULTY OF ELECTRICAL ENGINEERING AND COMMUNICATION

Master's Thesis

Master's study program **Microelectronics**

Department of Microelectronics

Student: Bc. Denis Misiurev ***ID:*** 186446

Year of study: 2 ***Academic year:*** 2020/21

TITLE OF THESIS:

Structural and electrical properties of PVDF-CNT composite

INSTRUCTION:

Theoretical part of this project will include overview of PVDF structure and its potential application in electronics. Description of existing PVDF fibers individual phases and their advantages should be mentioned. Literature review of the PVDF doping by CNT should be provided.
Practical part should consist of preparation of pure PVDF material and PVDF-CNT composite by electrospinning. Analysis of the pure PVDF and CNT doped PVDF fibers should be done. Performance should be studied by electrical measurement. Structure and phase composition and micromorphology should be studied by scanning electron microscopy, crossections by focused ion beam, Raman and Fourier transformed infrared spectroscopy. Evaluation of used preparation method, influence of process parameters on quality of the fibers should be presented in order to obtain complex information about influence of CNT doping to PVDF performance.
The outlook for further experiments should be given as well as comprehensive conclusions from the theoretical and experimental studies.

RECOMMENDED LITERATURE:

Podle pokynů vedoucího práce

Date of project specification: 8.2.2021 ***Deadline for submission:*** 25.5.2021

Supervisor: Mgr. Dinara Sobola, Ph.D.

doc. Ing. Lukáš Fujcik, Ph.D.
Chair of study program board

Abstract

Electrospininig has been proven one of the most popular and widely spreaded method of producing high quility of vibers with required parametrs. The quality and morfology of produced vibers is based on many parametrs such as humidity, doses of material, applied voltage etc.

Limitations of ceramic piezomaterials (brittleness, toxicity of lead-containing samples, difficulties of complicated shapes preparations, etc.) forced the research in the field of piezoelectric polymers. One of them is polyvinylidene fluoride (PVDF). It could be prepared in various forms: thin films, bulk samples, fibers. PVDF fibers attract the most attention because of high flexibility, lightweight, mechanical stability, chemical inertness. Properties of PVDF fibers can be tuned using dopant material: ceramic particles, metal nanoparticles, graphite materials as graphene oxide or carbon nanotubes (CNT).

Keywords

Piezoeffect, polarization, polymer, carbon nanomaterial, phase composition, electrospininig, Taylor cone.

Abstrakt

Electrospininig se osvědčil jako jeden z nejpopulárnějších a nejrozšířenějších způsobů výroby vysoce kvalitních vláken s požadovanými parametry. Kvalita a morfologie vyráběných vláken závisí na mnoha parametrů, jako je vlhkost, dávka materiálu, aplikované napětí atd.

Omezení keramických piezomateriálů (křehkost, toxicita vzorků obsahujících olovo, obtížnost přípravy složitých tvarů atd.) vynutila výzkum v oblasti piezoelektrických polymerů. Jedním z nich je polyvinylidenfluorid (PVDF). polyvinylidenfluorid může by být připraven v různých formách: tenké filmy, objemové vzorky, vlákna. PVDF vlákna přitahují největší pozornost díky vysoké flexibilitě, nízké hmotnosti, mechanické stabilitě a chemické inertnosti. Vlastnosti PVDF vláken lze zlepšit pomocí doplňujících materiálů: keramické částice, kovové nanočástice, Graphicitové materiály jako jsou oxid Graphicenu nebo uhlíkové nanotrubičky (CNT).

Klíčová slova

Piezoefekt, polarizace, polymer, uhlíkový nanomateriál, fázové složení, elektrospinin, Taylorův kužel.

DECLARATION

I declare that I have written the semestral project titled “Title of Student’s Thesis” independently, under the guidance of the advisor and using exclusively the technical references and other sources of information cited in the project and listed in the comprehensive bibliography at the end of the project.

As the author I furthermore declare that, with respect to the creation of this semestral project, I have not infringed any copyright or violated anyone’s personal and/or ownership rights. In this context, I am fully aware of the consequences of breaking Regulation S 11 of the Copyright Act No. 121/2000 Coll. of the Czech Republic, as amended, and of any breach of rights related to intellectual property or introduced within amendments to relevant Acts such as the Intellectual Property Act or the Criminal Code, Act No. 40/2009 Coll., Section 2, Head VI, Part 4.

Brno . . . . . .author’s signatur

ACNOWLEDGMENT

I would like to axpress my deppest gratirudes to my colleagues i had pleasure to work side by side during the accademic year: Mgr. Dinara Sobola, Ph.D, Ing. Tofel Pavel Ph.D, Ing. Eva Stastna, Ing. Trčka Tomáš Ph.D, doc. Ing. Klára Částková, Ph.D. I also thankful to my colleagues for providing assistans in producing and processing sampels of PVDF.

I appreciate for support of this work for Czech foundation Agency (GA 19-17457S).

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Contents

Chapter 1 Introduction

The main object of this study is based on comparing properties of pure PVDF material with PVDF–CNT composite. The most important aspect of the entire study is producing pure PVDF material using technology calls electrospinning, furthermore determent which parameter effect efficiency of produced material. Once material is produced it needs to be evaluated based on electric respond. Parameters of material which has the strongest respond among others will be used to produce composite based on pure PVDF material and Carbon nanotubes. By comparing pure PVDF and PVDF–CNT composite we will be able to prove whether Nanotubes has any effect on properties of PVDF or not.

Analyzation methods such as Fourier Transform Infrared Spectroscopy and X–ray Photoelectron Spectroscopy will provide detail information about single elements the Composite is consists of and phases of PVDF.

Morphology of the produced material will be evaluated by method calls Focused Ion Beam there fibers of PVDF will be cutted by Ion bean.

Chapter 2 Polyvinylidene Fluoride polymer and Carbon Nanotubes

2.1 Polyvinylidene Fluoride

2.1.1 Characterization of Polyvinylidene Fluoride polymer

Polyvinylidene Fluoride (PVDF) is a semicrystalline, non–reactive Thermoplastic that is approximately fifty presents amorphous. The Percentage of crystallinity is based on the Chain ordering defects. PVDF is a Plastic material belongs to fluoropolymer family [1].

Polyvinylidene Fluoride (PVDF) is high purity thermoplastic fluoropolymer. PVDF is readily melt–processible and can be fabricated into parts by injection and compression molding [2].

Thanks to its excellent combination of properties and processability, PVDF has become the largest volume of fluoropolymers after PTFE.

PVDF is available commercially in a wide range of melt flow rates and with various additives to enhance processing or end use properties.

The atomic structure of PVDF is represented by monomer $-CH_2CF_2-$. The molecular weight of the monomer is between 16 and 17 kg/mol.

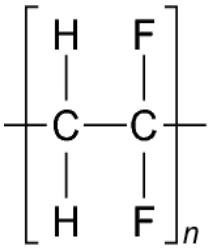


Figure 1. Molecular structure of PVDF [3]

The monomer $-CH_2CF_2-$ has strong electrical dipole moment with regards to electronegativity of fluorine atoms. The monomer forms chains with perpendicular orientation of dipole moments. The PVDF's properties, as with most polymers, has been intensively studied. The main focus of research has been done on two most important aspects, the thirst is polymorphism and second is piezoelectronic respond [4].

PVDF is semicrystalline material crystallized into different crystal phases: α (phase II), β (phase I), γ (phase III), δ, ε obtained by different process parameters [1]. Five polymorph phases of PVDF [5].

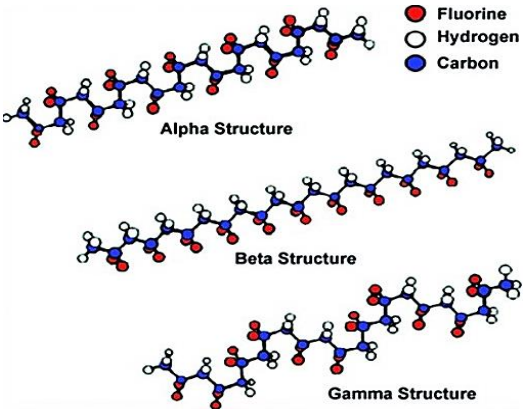


Figure 2. Common phases of Polyvinylidene Fluoride material [6]

The most stable at room temperature α phase is commonly synthesized among other phases, although the α phase is electrically neutral (non−polar), because of its antiparallel dipoles' alignment [1]. Phases I, III and δ show signs of electroactivity [7].

After applying mechanical stretching of alignment, high pressure, changing temperature of crystallization of melt the α phase can be transferred into oriented β phase [2]. The β phase is the most important due to its superior electrical, ferro−electrical and pyro−electrical properties in compare to other phases. Has been found the β phase not only represents huge potential due to the strongest piezoelectric respond among all PVDF's phases, but also the PVDF itself has the strongest piezoelectric response amongst all commercial polymers.

The polymer has many electronic applications, especially as jacketing materials for plenum–rated cable used in voice and video devices and alarm systems. The low flame spread and smoke generation of PVDF is a prime asset in these applications.

Emerging applications of PVDF include fuel cell membranes, and components for aircraft.

PVDF represents extraordinary mechanicals and chemical parameters such as:

- Deformation resistance
- Absorption resistance
- Chemically resistant
- Stability to radiation
- High working temperature (from –49° to 302° F)
- Electrical insulator
- Radiation stability

- High Curie point (217.4° F)
- High purity

Such combination of properties makes PVDF useful for varieties of application where the polymer is used in:

- Aerospace
- Biosensors
- Biotechnologies
- Pharmaceutical
- Microelectronics
- Pressure sensors
- Insulator for batteries

Well−characterized properties make the PVDF leader of piezoelectric polymers.

2.1.2 Synthesis of Polyvinylidene Fluoride material

PVDF represents excellent chemical, thermal stability. As a result of this properties the PVDF is promising and environment friendly material to produce membranes from. [8–10]

The most popular PVDF material is represented by nano/microfibers, since it is easiest way to use produced fibers in wide range of applications right away. Nevertheless, there is another type of material, which has been proven useful in nowadays. PVDF membranes or films are used in medicine and industrial in recent years due to unique combination on properties and high chemical resistance.

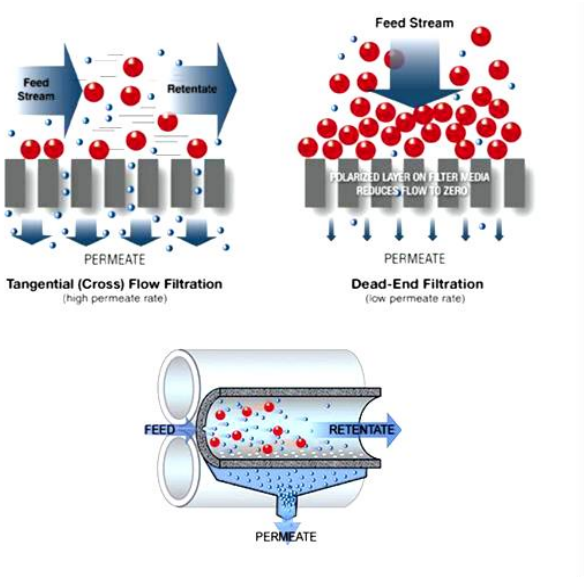


Figure 3. Schematic representation of PVDF membrane [11]

Commercial PVDF membranes show outstanding strength and mechanical resistance. Thanks to high dissociation energy of C–F chains, produced films represent extraordinary thermal stability. Solubility of PVDF allows to produce wide range of geometry form. Chemical compatibilities of PVDF allows to modify produced membranes to enhance chemical resistance and performance. One of the major disadvantages of produced PVDF membrane is hydrophobic nature of polymer. Membranes always face trouble wetting the membrane by water and highly absorption of foul during filtration, which cause raise of expansions cost of PVDF membrane. To solve the problem PVDF polymer require modification. Polyvinylpyrrolidone has been proven useful addictive to relieve the issue. Effective pore−forming addon PVP has found effective in producing manufacturing membrane [12].

PVDF membranes are produced by different methods such as phase inversion, sintering, track etching. Phase inversion is the most popular method to produce PVDF membranes for industrial sector due to simplicity in nowadays.

In the method homogeneous precursor solution is transformed into a solid state. The most important phase of entire process, which is determining the morphology of the produced membrane is the initial state of phase inversion. Produced by this method membranes have asymmetric structure [12].

The method is divided into who different sub methods. Thirst is thermally induced phase separation (TIPS). Second is immersion precipitation (IP) [12].

TIPS stands for slow, thermal evaporation of the solvent from PVDF melted precursor creating membrane [12].

In the Immersion precipitation method precursor is coated on non–solvent and located in a coagulation bath. Solid membranes are produced as a result of mass transfer between polymer−solvent–non−solvent system [12]. The diagram represents relationships between nonsolvent–polymer−solvent which is described in 4 paths.

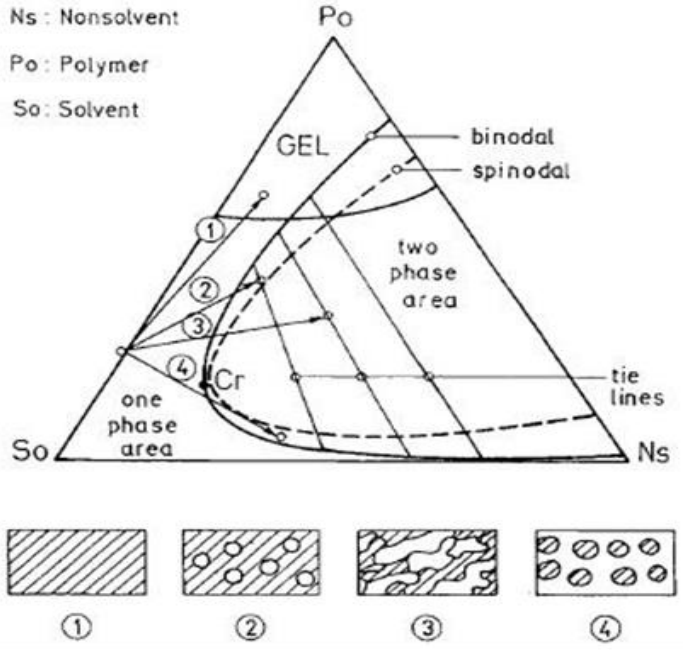


Figure 4. Ternary diagram nonsolvent/solvent/polymer [12]

2.2 Carbon Nanotubes

2.2.1. General overview of Carbon Nanotubes

Carbon nanotubes are unique carbon fibers with similar structure of fullerene. As other unique properties have been discovered such as remarkable mechanical and electronic properties unique Roman spectra, thermal conductivity, toughness, interest to nanotubes started to grow and their potential use in wide varieties of applications especially in nano–dimension electronics and medicine [13].

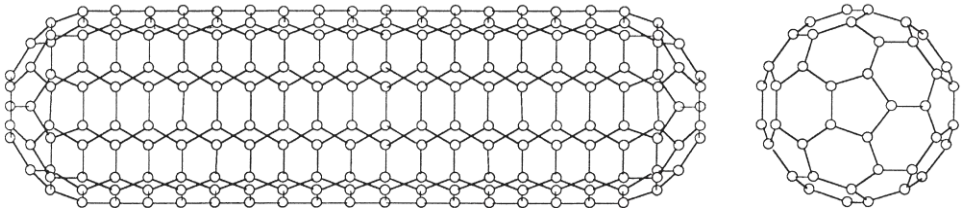


Figure 5. Structure of nanotube [13]

The structurer of carbon nanotubes is similar to structure of 3D (Figure 5) graphite and memorize honey camp. An ideal nanotube represents hexagonal network of carbon atoms rolled up to form seamless cylinder. These cylinders are represented by layers of fullerene molecules.

Base on presence of this layer nanotubes can be divided into subcategories: single−walled nanotubes (SWNT) (Figure 7), double walls nanotubes and multi−wall nanotubes (MWNT) (Figure 8) [14].

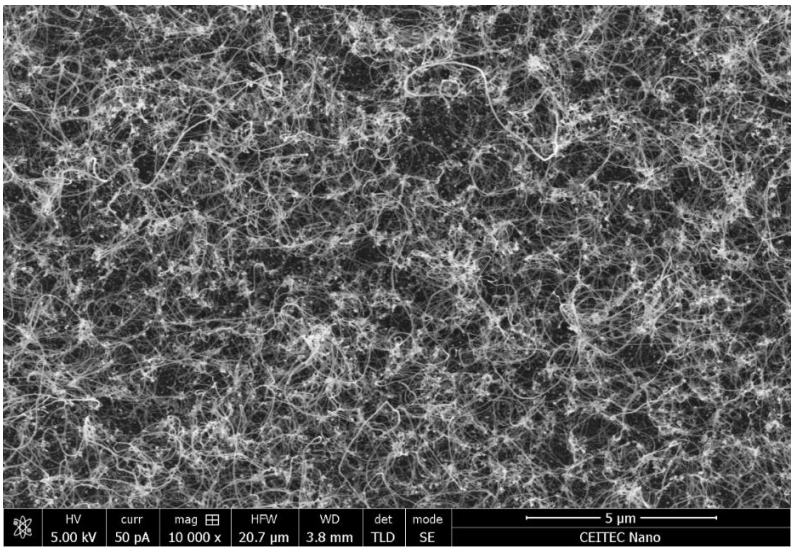


Figure 6. Produced nanotubes

2.2.2. Structure characterization of nanotubes

Nanotubes are subdivided on two types: single−walled nanotubes (SWNT) and multi−wall nanotubes (MWNT).

Single−walled nanotubes have only one−layer thick shell, this can be considered as the fundamental structure. This structural unit serves as a building block for multi−wall nanotubes, contained multi coaxial with increasing diameter of cylinders [13].

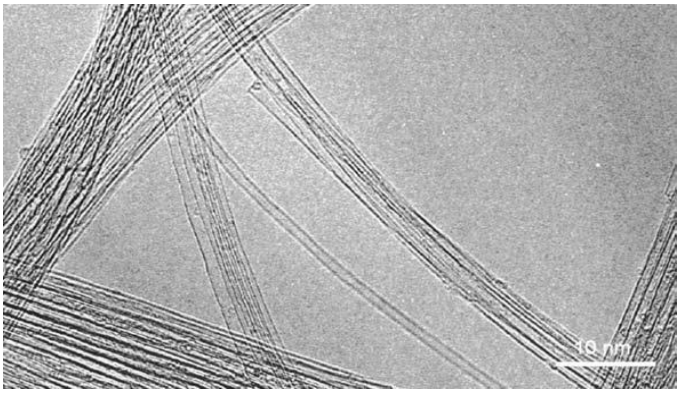


Figure 7. Single−walled nanotubes [13]

SWNTs have properties of metallic, semi−metallic, metallic wire depending on structural parameters, diameter and chirality. Huge effort has been done to study their mechanical properties. Typical diameter of Single–wall nanotubes is within 1 nanometer (nm). It could be rather difficult pro produce SWNT since the process require keep and adjust working parameters on very precise level. The most popular method of producing SWNT is Laser Ablation Method [13].

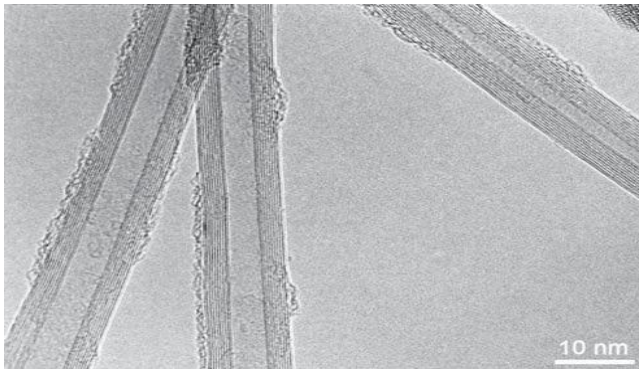


Figure 8. Multi−wall nanotubes [13]

Multi–walled nanotubes (MWNT), consisting of several single wall nanotubes nested inside one another. MWNTs have less stable CNT compare to SWNTs because of their inbuilt structural defects and undefined diameter [14].

Properties of MWNT are similar to SWNT since SWNT are building block for MWNT, however they are less prominent due to amount of defect occurring during producing process. There is variety of methods to produce effectively produce MWNT in high quantity and good quality such as Chemical Vapor Deposition (CVD), Arc Discharge Process [13].

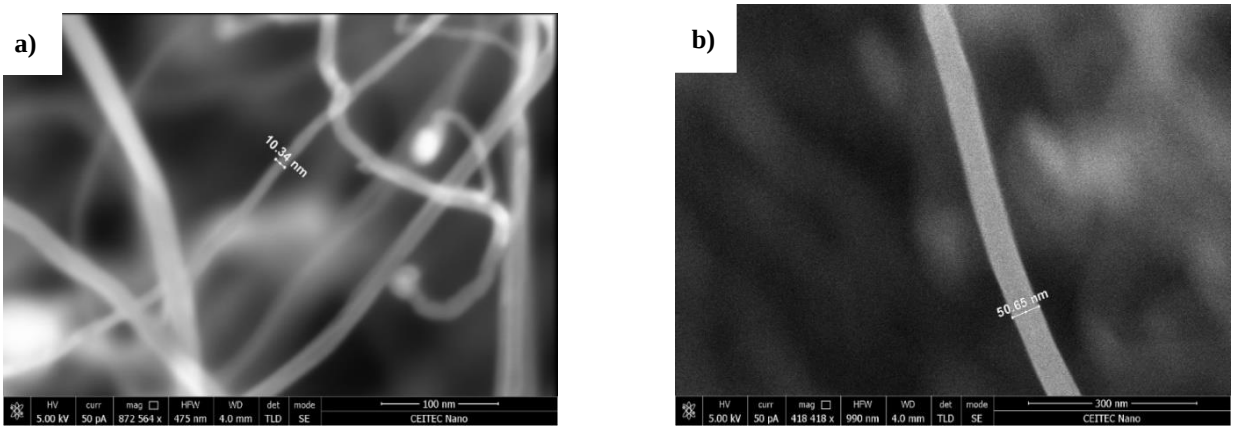


Figure 9. a,b) Different diameter of produced nanotubes

2.2.3. Technology of producing nanotubes

The most effective method to synthesis single wall–nanotubes is used Laser Vapor Evaporation. The apparatus of the method is used neodymium–yttrium–aluminum–garnet (Nd:YAG) laser to vaporize a graphite target located in a tube. The target is doped by impurity approximately 0.5–1% of cobalt or nickel. Metals such as iron, chrome serve as a catalysator as well. The impurity is served as catalysator for growing nanotubes [15].

The laser heating up the target to temperature around 1200–3000°C with creation of carbon vapor. Evaporation is done with present of inert gas in tube of diameter of 5 cm usually with argon or helium at pressure 500 torr. Flow of inert gas through tube to transfer the soot generated to a water-cooled copper collector, the quartz tube walls, and the backside of the pellet. [15] After evaporation carbon vapor comes into interaction with the cooled counter electrode and condensed on it forming single–wall nanotubes. Synthesized nanotubes are scrapped off from collector. The method is allowed to produce roughly 1 gram of SWNTs powder. The resulted nanotubes are highest quality and purity. Using the method both types of nanotubes are obtainable. Produced nanotubes are represented in form of ropes with diameters of 5–20 nm and micrometers long [15]. The main disadvantages of the method are focused on productivity of the method. Using laser in continence mode will increase creation of carbon vapor, thus productivity of the process, however the mode requires huge energy consumption.

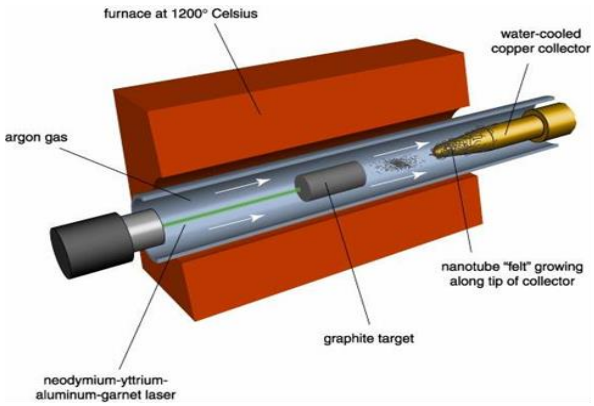


Figure 10. Representation of Laser Vapor Evaporation [15]

Multi–walled nanotubes are obtained by using controlling grow under certain conditions such as keeping melting temperature of carbon to create carbon vapor, with presents of inert gas usually argon or helium [15].

The method called Arc Discharge allowed produce straight MWNT. Method is not used much often in nowadays due to high energy consumption.

Main chamber is 30 cm in diameter wight cylinder usually in 1 m long. At the beginning of process, the vacuum is created in main chamber under pressure 0.1 Pa, then main chamber is filled up by inert gas. Electrodes are represented by graphite rods, anode is 6 mm diameter and cathode is 9–13 mm. The cathode is cooled by water to speed up synthesis of nanotubes on the surface of cathode. In this apparatus carbon electrodes are located in close distance to each over while arcing process running. Electrodes are mothing even closer during process, however the working distance is maintained roughly 1 mm. To create arc discharge stabilized DC power supply is required and voltage is around 20V. Current flowing between electrodes in range of 50 up to 100A. The temperature of discharge reach 4000°C which allowed to etch of carbon electrodes and creating vapor. The vapor interacts and condensates on cathode forming straight, cylinder multi wall nanotubes [15].

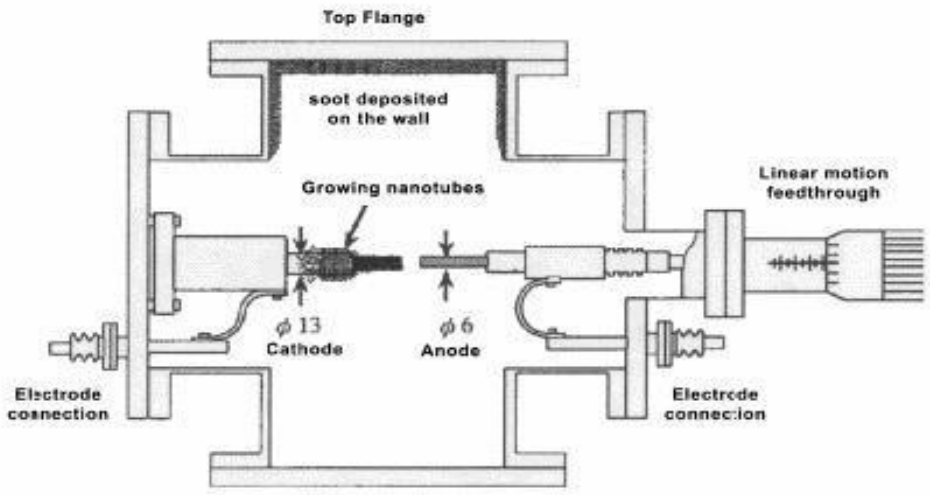


Figure 11. Arc discharge main reactor [15]

The diameter of resulted MWNT is within range of 30 nm and approximate length is 1 μm. Each MWNT has 2–50 coaxial single wall nanotubes within the structure. Large range of nanotubes are produces at applied potential of 18V DC with presence of helium and pressure 500 torr. This method does not require catalyze impurities in order to initiate process [15].

The structure of nanotubes is strongly related to manufacturing parameters such as temperature, inert gas flow, pressure etc. Defects effects electrical, mechanical properties [15].

The technology allowed to produce large quantity of nanotubes. However, the arc discharge has high amount of defects accruing during process. Produced nanotubes require purification because of presence of catalysator [15].

Chapter 3 Samples preparation

3.1 Chemical Vapor Deposition of Carbon Nanotubes

The chemical vapor deposition is the most popular method has been successfully used in producing nanotubes [16]. Main principle of the method is based on thermal grow of nanotubes, both SWNT and MWNT, with presence of carbonic gas and hydrogen on substrate with catalyst metals such as iron, nickel, cobalt etc. The catalyst helps carbonic gas to decomposed and create carbon atoms, base for future nanotubes. Carbon atoms are key elements of growing carbon nanotube.

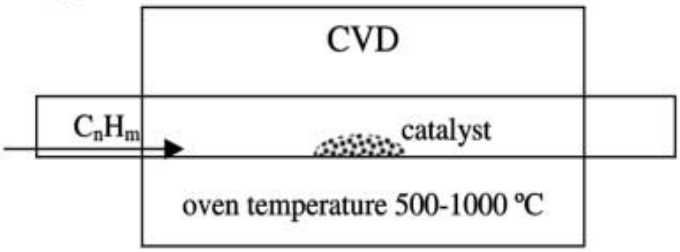


Figure 12. Chemical Vapor Deposition schematic representation [16]

Carbon atoms laying down on top of catalyst film and start growing nanotubes. For MWNT synthesis CVD methods use ethylene or acetylene as working gas to initiate growing process [16]. MWNT are produced at low temperatures usually around 300–800°C with [15] presents of inert gas. Has been found SWNT are produced with higher temperature about 600–1150°C [15] with presents of inert gas mixed with hydrogen.

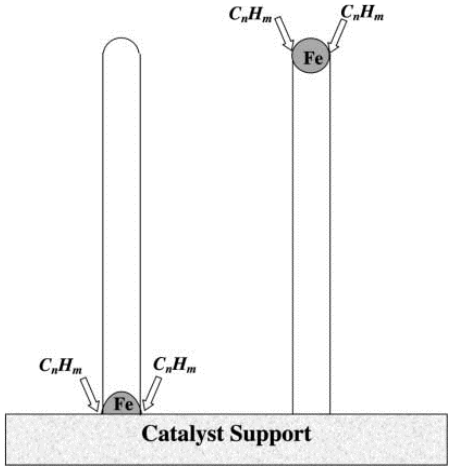


Figure 13. Base grow, top grow nanotubes mechanism [16]

Nanotubes mechanism of growing can be described in two different models: base grow, there nanotubes are growing on top of catalytic film, top growing, there nanotubes are growing underneath atoms of catalytic film [16].

Nanotubes are not only the product of the process but also material such as polyhedral, aromatic, amorphous carbon, metal particles, etc. are by–products acquired during the process [15].

A major undertake of CVD method has been found in high probability of MWNT structure defects. The nature of defects is still not enough studied, it is highly likely caused by low temperature of growing nanotubes, which does not provide enough energy to sufficiently transform carbon atoms into perfectly linearized structures [16].

3.1.1 Electron Beam Physical Evaporation Deposition of 5 nm Iron Catalysator Thin Film

To initiate grow of carbon nanotubes thin film of catalysator metal is required. Metals such as iron, nickel, cobalt, titan can be used as catalysators, however thickness of coated film will be different based on recipes. The catalysator film is required to provide addition support of decomposing of hydrocarbon gas to carbon atoms and start formation of nanotubes. To start formation of nanotubes 5 nm of iron film is required according to recipe.

Electron Beam Physical Evaporation is popular technology is used to obtain films of required material in substantial quality and properties [17].

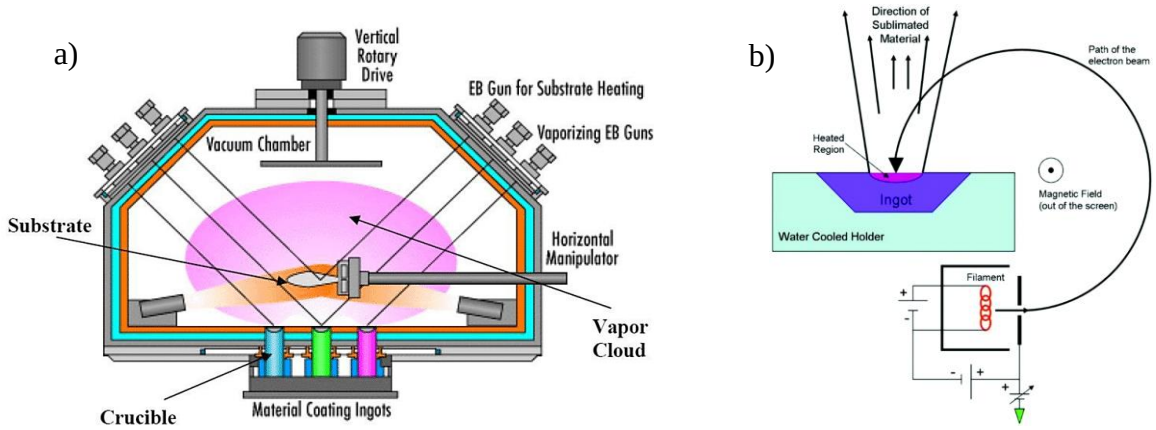


Figure 14. a,b) Main chamber and schematic representation [18],[19]

Electron beam [20] is highly versatile method. Using this method huge varieties of material can be evaporated. [21]

The system uses highly energetic electron beam to vapor targeted material [22] with present of vacuum [16]. The vapor [22] condensates on cooler surface or component creating of deposit, coating. External heating sometimes applied during process, to enhance formation of metal–surface coating [16].

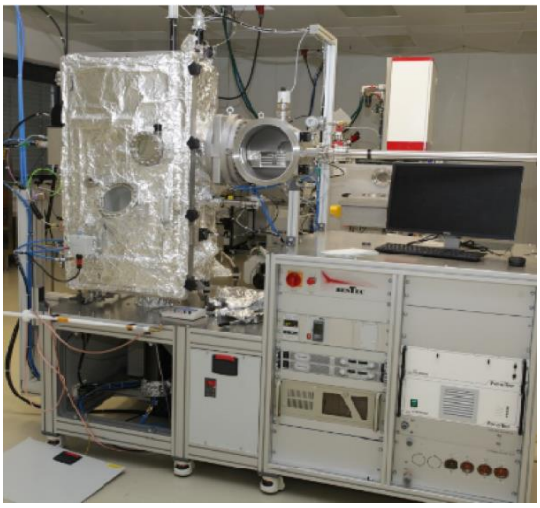


Figure 15. Evaporator system located on CEITEC Nano [23]

The materials for coating have to reach high pureness to avoid any signs of possible impurities or contamination of resulted film. The electron beam gun source allows to achieve very high deposition rate. Deposition rate is within 20–30 μm per second [23]. Thickness of the resulting of coating is controlled by crystal. The crystal is vibrated with certain reference frequency, during process evaporated material condensates not only working surface but also all surroundings within the chamber. The condensed material coasted drop of reference frequency of the crystal. By measuring the difference between frequencies, the thickness of the resulted can be determent.

Physical Evaporation Deposition technique is used in huge variety of applications from decorative to coating superconductive films. The technique is allowed to produce film from one atom thick to millimeters [23].

3.1.2 Plasma Enhanced Chemical Vapor Deposition of Multi–Wall Nanotubes

Plasma Enhanced CVD (Chemical Vapor Deposition) is a variation of the CVD, where inert gas plasma is used to produce thin films. The technique has been developed to produce not only wide variety of organic and inorganic films but also Aligned Multi–Wall Nanotubes of high quality, which do not require additional purification from by–products.

Plasma Enhanced CVD (Chemical Vapor Deposition) consist of 2 steps: catalysis treatment and grow step. The first step involves preheating of working medium [24]. As a working medium usually used hydrocarbon gases (ethylene or acetylene) and hydrogen mixed with hydrocarbon gas.

Figure 16. PECVD system located on CEITEC Nano [25]

The main reactor can operate in two different modes: closed and opened. The open mode is more popular in nowadays. During the process substrates with catalytic film are located in container. The container is closed and placed in the main chamber of the reactor. The chemicals continuously entered the main chamber of reactor under controlled pressure. The Plasma Enhanced CVD require external, high activation energy to start formation of inert gas plasma and pressure to maintain plasma. Ionization energy is extremely high, which cause limitation of the method. Unlike in CVD, chemical reactions in PECVD method are performed under low temperature (300–800°C). Reactions are activated by plasma. Then chemicals are entering into main reactor, plasma decomposed chemicals and break chemical bounds turn them into free radicals and ions. [15] Neutral molecules become polarized and chemically active thanks to high

energy of plasma. Free radicals and ions in gas phase are bombarding the surface of growing film and create dangling bonds [16].

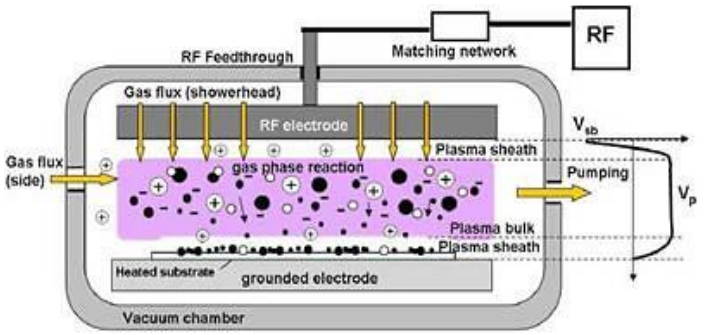


Figure 17. PECVD Process of producing nanotubes [26]

Multi–Wall Nanotubes has been produced on 5 nm thick iron film silicon substrates and according to followed recipe:

1) Pumping for 30 seconds.

Main chamber of the reactor must be cleaned from any particles to avoid possible contamination resulted nanotubes.

2) Heat up to 750 °C, 1000 mTorr (Torr is 133.3224 Pa), Ar 1000 sccm (Standard cubic centimeters per minute), transfer sample into the main chamber at 695 °C.

Main chamber needs to heat up to increase reactivity of poring chemicals and create appropriate pressure in it. Substrates must be interred into main chamber heated to avoid heat stress with presence or inert atmosphere.

3) H_2 Stab, 750°C, 1 min, 1000mTorr, H_2 200 sccm.

Poring certain amount of hydrogen into main reactor at same temperature as main reactor under defined pressure.

4) H_2 pretreatment, 750 °C, 10 min, 1000 mTorr Ar 1000 sccm + H_2 200 sccm

Mixing hydrogen with inert atmosphere.

5) Growth, 750 °C, 30 min, 1000 mTorr, Ar 1000 sccm + H_2 200 sccm + C_2H_2 20 sccm

Initiation of growing process with presence of hydrocarbon gas mixed with hydrogen.

6) Cooling down, 1000 mTorr, Ar 1000 sccm, transfer to loadlock <695 °C, after that cooling down without Ar, 1000mTorr

Hot substrates are transferred back into loadlock and cooling down without present of inert gases.

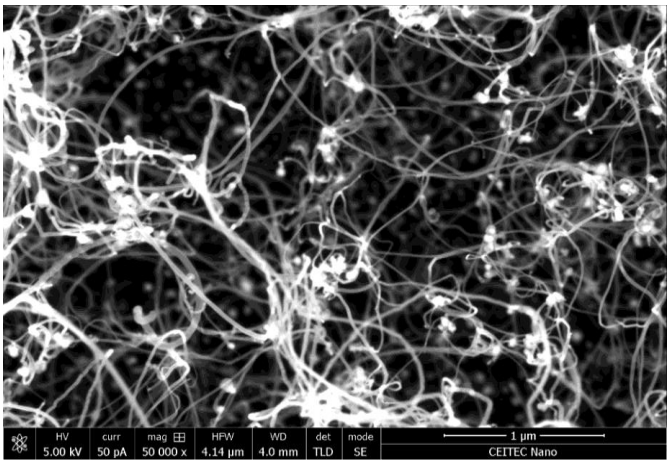


Figure 18. Produced nanotubes using PECVD method

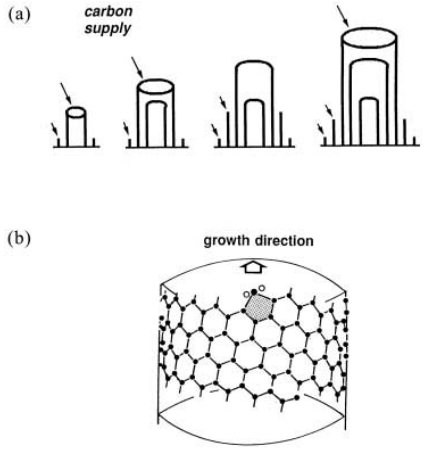


Figure 19. a,b) Growing mechanism of multi−wall nanotubes [27]

Plasma contains electrons and ions possessing energies that can break chemical bonds. Therefore, electron-molecule collisions create radicals in the gas phase and ions bombarding the surface of growing film activate the surface by creation of dangling bonds. The ions also help to densify the growing film by etching a weakly bonded terminating group.

The advantage of PECVD is electric field which is formed within a plasma. Developing of electric field allows to adjust formation of CNTs [14].

3.2 Electrospinning of Polyvinylidene Fluoride

3.2.1 Process foundation

There are many available commercial technologies of producing Nanofibers, however there is one technology which allow produce fine fibers [28].

Electrospinning is unique self–assembly technology offers wide variety of adjustable parameters to produce required fibers. Electrospinning is the thirst technology allowed to produce fibers which formation is given by electrostatic forces rather mechanical. Fibers obtained by using electrospinning are self–organizable [29]. Thanks to rather not completable basic setup, producing huge range of nanofibers and controlling their morphology by changing process parameters the electrospinning gained huge popularity and widely used in nowadays [28].

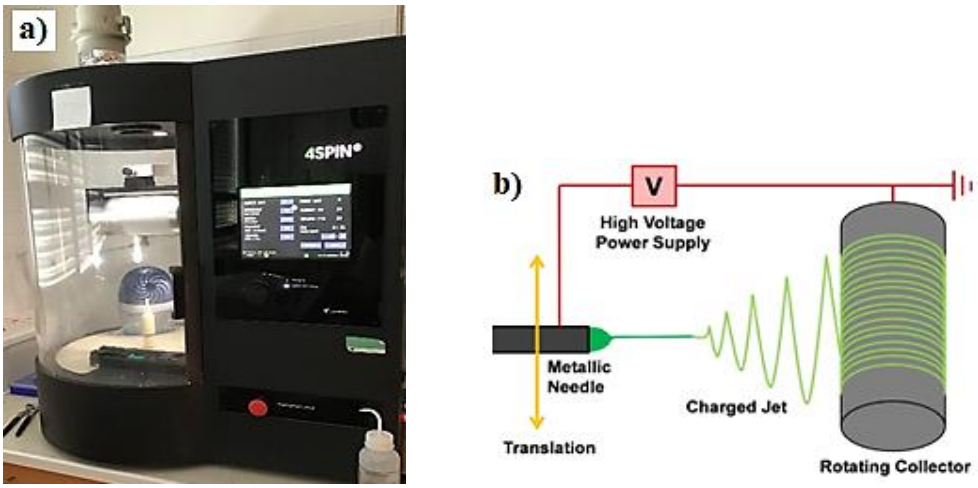


Figure 20. a,b) Electrospinning machine 4SPIN, schematic representation [30].

The basic setup is rather simple consisted of two counter electrodes and DC voltage supply applied on needle−based electrode [29]. One of the counter electrodes is represented by metallic needle, the second, however, can be different one based on application the fibers are produced for. The most popular is cylinder counter electrode because of its simplicity. To simplify cleaning counter electrode and removing produced fibers the counter electrode is covered by foil of conductive material. Simple Aluminum foil is one the most spreader conductive material is used for electrospinning. In order to transport precursor (melted polymer) the certain approach is required [28]. It has been found experimentally a tiny, silicon tube and commercial, medical syringe are perfect to transport precursor into metallic needle and then start the spinning of nanofibers [28].

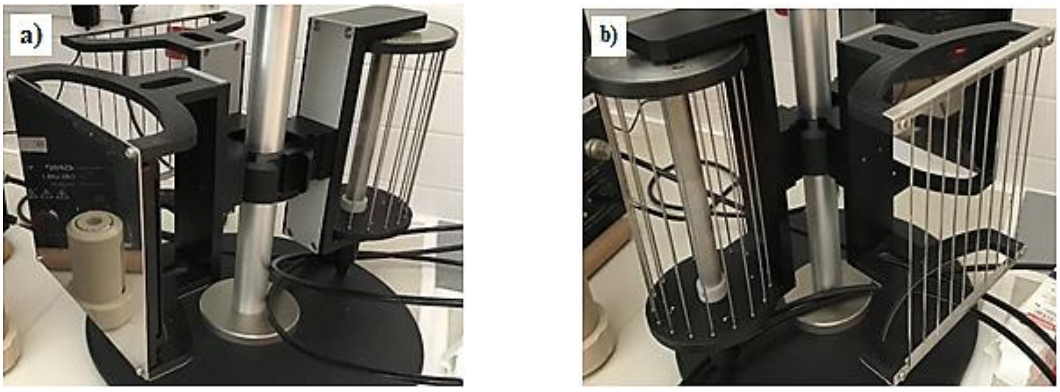


Figure 21. a,b) Different varieties of counter electrodes

To annihilate the process itself is needed to set up working parameters according to corresponding recipe of polymer to make fibers from.

Parameters in most cases are given as followed [28]:

- Working Distance between counter electrodes: 8–20 cm
- Applied DC voltage: 0–60 kV
- Polarity of electrostatic field: positive
- Ability to use Hot Air: Temperature: 50–100C°, air flow: 0–50 l/min
- Number of rotations: 0–3000
- Needle diameter: 0.1–1 mm

Hot Air mode is used to speed up drying process of solvent, thus it will help to avoid popular defect of commercial fiber – thickened drops of precursor.

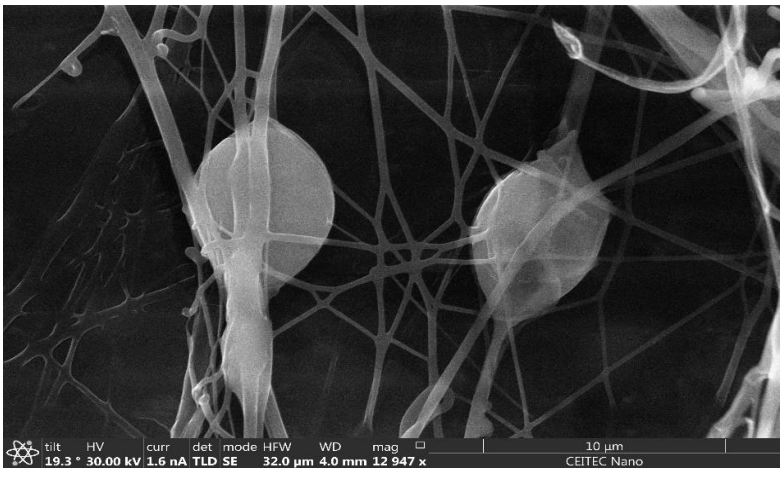


Figure 22. Defect calls thickened drops of precursor (PDVF + CNT)

The spinning process is starting by transporting precursor from medical syringe into metallic needle. Small drop of precursor starts to form on the top of the jet (needle). At this moment with applying electrostatic field so called Taylor cone starts to appear. Within the cone fibers are transforming from liquid precursor into solid fibers by drying of solvent and, in case of PVDF, become polarized. Formed fibers are collected on rotating counter electrode.

It takes a lot of practice and calibration of working parameters to produce high quality fibers with required thickness of fibers and morphology [31]. Calibration cannot be performed without spending material. Electrospinning allows to spend minimum amount of materials to reach best possible processing conditions which could be critical dealing with non–organic precursors due to high cost.

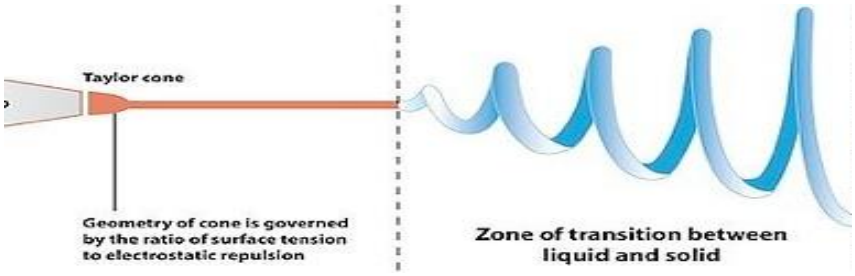


Figure 23. Taylor cone [32].

At the end of process, the Aluminum foil must be carefully removed from counter electrode to do not deformation of the foil and fibers themselves.

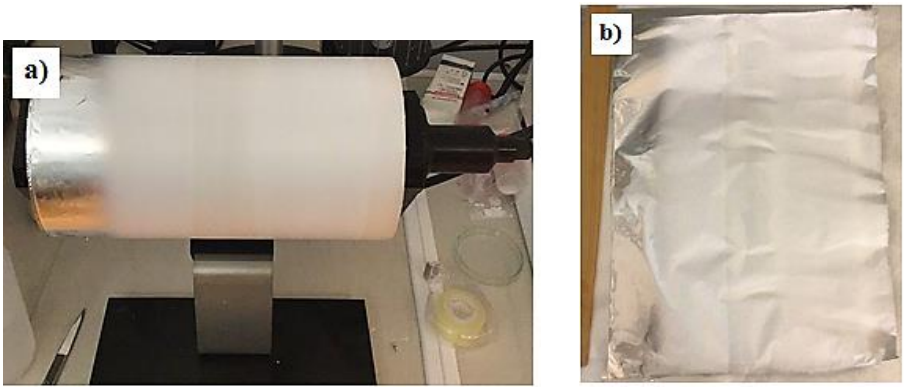


Figure 24. (a) Removed counter electrode with produced fibers, (b) Removed Aluminum foil

There are many parameters what dramatically effect quality, morphology, and orientation of produced fibers. Changing at least one of them could involve calibration of other processing conditions.

Parameter	Increasing	Decreasing	Orientation	Morphology	Quality
Working Distance (WD)	There is strong possibility fibers will not be collected on counter electrode.	With decreasing WD the solvent in precursor will not dry out completely, thus thickened drops of precursor will accrue (Figure 20), furthermore fibers will not be properly formed.	With decreasing working distance.	It appears, that with decreasing of WD, still wet precursor collects even more fibers around itself which leads to creation thickened clusters of fibers.	Thickened drops defect that appears at small WD can significantly lower piezoelectronic and triboelectric effect due to its electroneutrality.
Voltage	High voltage causes stretching of Taylor cone by higher generated charge which leads to faster formation of fibers from smaller amount of precursor [31].	Lover voltage shrinks Taylor cone, thus bigger amount of precursor can easily degrade on the top of needle and compromise entire process by clogging of needle [31].	Does not change	With increasing voltage produces fibers become thinner. In case of successful formation [31].	Both thick and thin fibers are used in different applications.
Number of rotations	By increasing numbers of rotation counter electrode more fibers are produced.	With lower number of rotations less fibers are produced.	High number of rotations allowed to produce oriented (parallel) fiber; chaotically orientated fibers are produces by lower number of rotations.	The morphology of parallel and chaotically fibers is pretty much same.	In some cases, with high number of rotations, produced fibers have tendention to create areas with nonhomogeneous thickness of produced fibers, although fibers produced by lower number of rotations have homogeneous thickness.
Needle diameter	There are few studies about effect of needle diameter on electrospinning; It has been proved needles with smaller diameter clogging less often rather with bigger one. By using Scanning Electron Microscopy has been proven, fibers produced by using needles with smaller diameter have tiniest diameters and vice versa. However, in different cases has been found no correlation of fibers and needle diameters [3].				
Precursor viscosity	It is important to temper precursor on the right temperature in order to lover its viscosity since the viscosity of untempered precursors is high. Precursors with high viscosity will not be spined at all, even such precursors like PAG (nylon) have to be tempered to makes the spinning process possible. Tempered precursor has lower tendency to clog up the needle and speed up formation of fibers while the spinning process is running.				

Table 1. Summarization of processing conditions on produced fibers

The table 1 represents parameters which effect the produced material. The effect of singe parameter has been defined experimentally. To determent if there are any changes in

Morphology of the produced material the morphology has been studied using Scanning electron Microscopy (SEM).

The orientation of produced fibers is represented in two different ways: oriented and non-oriented. The orientation of produced fibers is given by amount of rotation per minute the fibers are collected on counter electrode. During the process, fibers formed within Taylor cone are collected on counter electrode. If the amount of rotation is not high enough produced fiber are suspended under the needle and slowly collected on counter electrode creating chaotically orientated thin film.

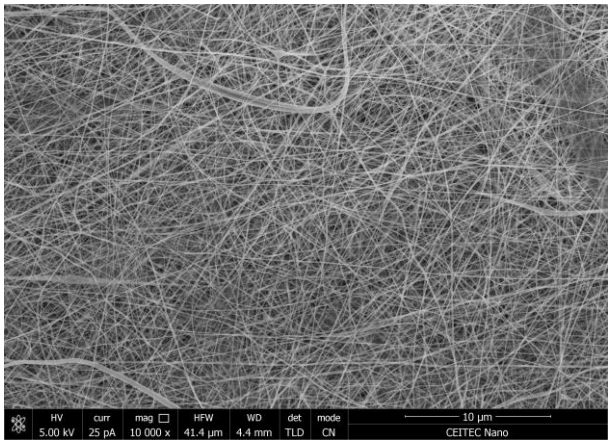


Figure 25. Sample of Nylon nanofibers

If the number of rotations is high enough produced fibers are not suspended under the needle and collected on counter electrode mostly immediately and create in most cases clusters of orientated fibers.

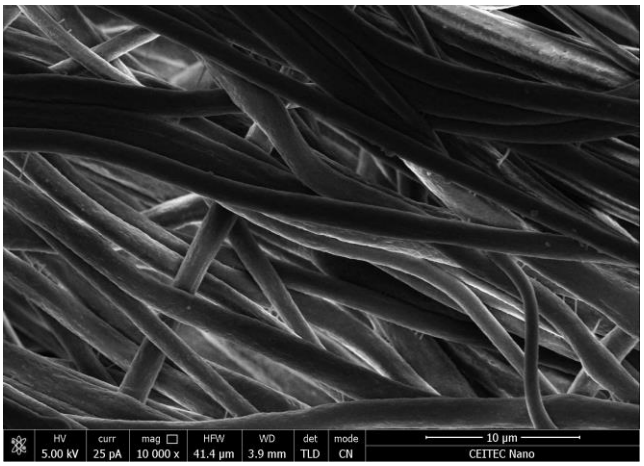


Figure 26. Sample of Pure PVDF Microfibers

To obtain orientated fiber the number of rotations per minute must by more than 1000 rotations and less than 500 to produce non oriented fibers.

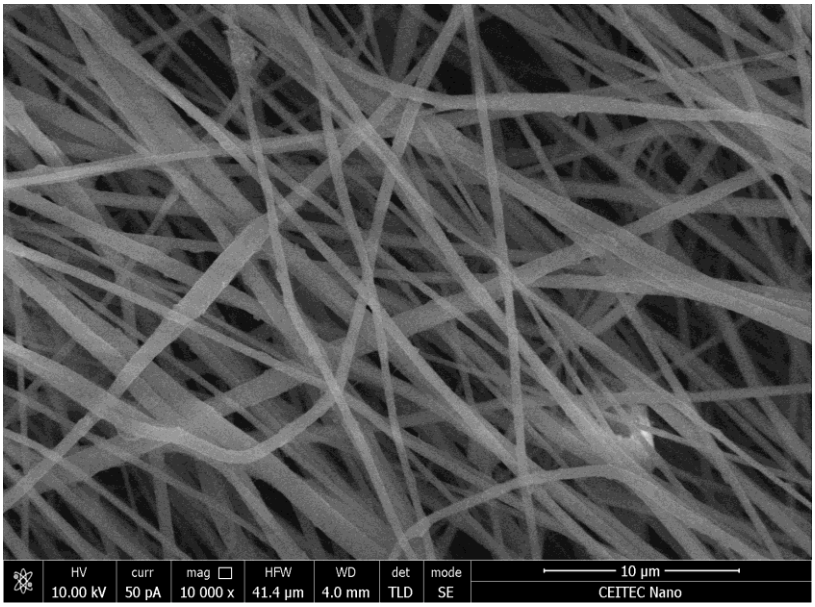
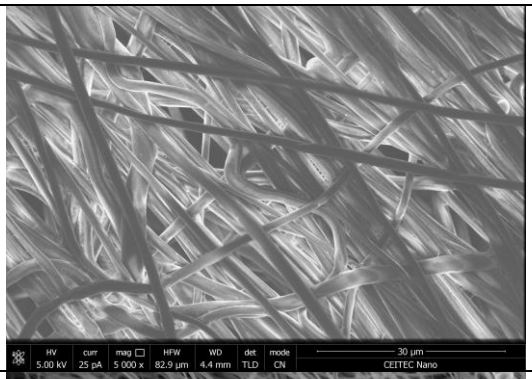
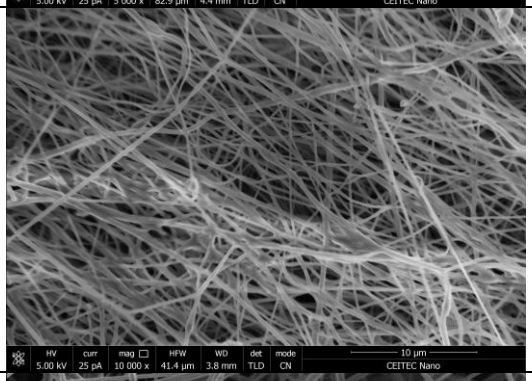
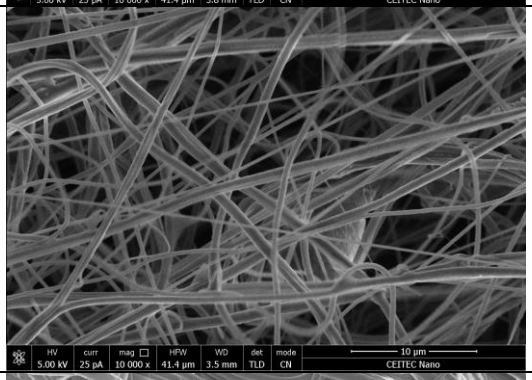
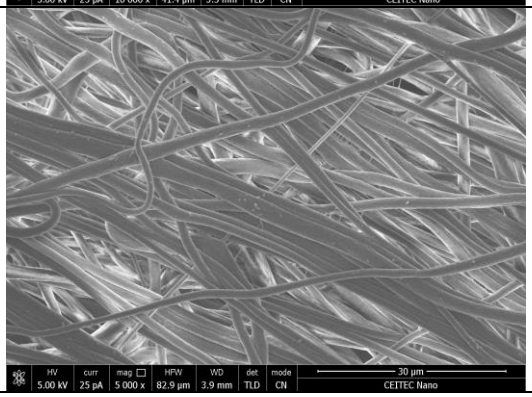


Figure 27. Sample of PVDF–CNT composite (20–20)

Hot Air can be essential in cases where precursor is rather old, badly spined, watery. Hot Air is used not only to speed up drying precursor solvent by lowering humidity and helps to avoid the most popular defect calls “thickened drops of precursor” (Figure 22) but also improve quality and properties of produced fibers.

Sample №	Parameters	Average fibers diameter (μm)	SEM image
29–1,2	Precursor: PVDF 20% 275 WD: 20 cm Doses: 40–50μl/min Voltage: 50kV Humidity: 30–>20% Rotations: 2000 min^{-1} Hot air mode: On Process duration: 120min	1.7	
29–3	Precursor: PVDF 20% 275 WD: 20 cm Doses: 20–30μl/min Voltage: 50kV Humidity: 30–>20% Rotations: 2000 min^{-1} Hot air mode: On Process duration: 90 min	0.464	
29–4	Precursor: PVDF 15% 275 + CNT WD: 20 cm Doses: 20–25 μl/min Voltage: 50kV Humidity: >30% Rotations: 1000 min^{-1} Hot air mode: On Process duration: 90min	0.664	
29–5	Precursor: PVDF 20% 275 WD: 20 cm Doses: 40–50μl/min Voltage: 50kV Humidity: 30–>15% Rotations: 2000 min^{-1} Hot air mode: On Process duration: 120min	1.7	

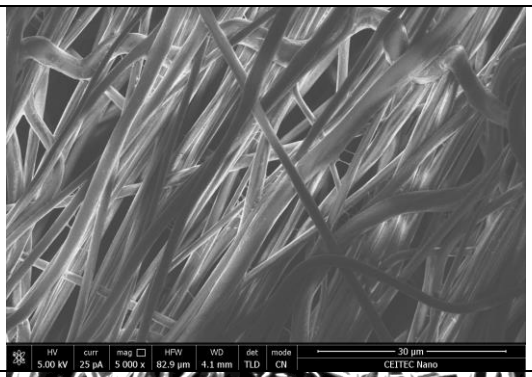
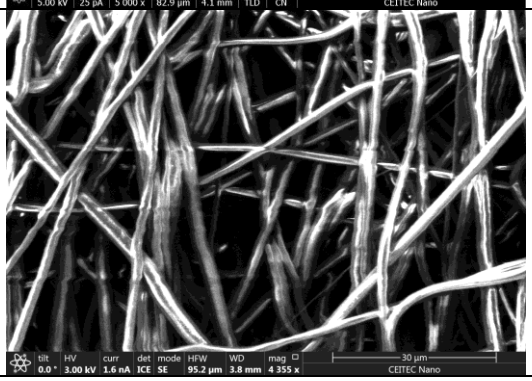
29–6	Precursor: PVDF 20% 275 WD: 20 cm Doses: 40–50µl/min Voltage: 50kV Humidity: 30−>15% Rotations: 2000 min^{-1} Hot air mode: On Process duration: 120min	2	
29–7,8	Precursor: PVDF 20% 275 WD: 20 cm Doses: 40–50µl/min Voltage: 50kV Humidity: 30−>15% Rotations: 2000 min^{-1} Hot air mode: On Process duration: 150min	2	

Table 2. Summarization of produced fibers

The table 2 contains summary parameters of produced samples. It has been proven that with increasing doses of precursor the average diameter of producing fibers increase as well.

3.2.1 Influence of humidity on surface morphology of produced fibers

Humidity is vitally important if it comes to electrospinning and initiation of producing fibers. If percentage of humidity is too high the initiation of fiber formation could not get occur because of excess water which did not dry out fast enough to form Taylor cone. If there is extra low humidity or even vacuum in the main chamber of electrospinning machine, low humidity can jeopardize the initiation of process. Solvent will dry out extremely fast within low humidity atmosphere which could lead to clogging of needle. According to observations the humidity has much more influence on surface morphology above all other parameters. Humidity indicates the amount of water which will be on surface of fibers until it dries out.

It has been proven that fibers produced with lower humidity has lowest amount surface defect and electrospinning process runs much more smother compare to high humidity condition.

Fibers produce within relatively high humidity > 50 % have rough surface because of slowing drying process of solvent and water vapor. Rough surface of produced fibers cause lowers performance in terms of electric and triboelectric respond because of lower interaction between fibers though surface.

Interaction of fibers though surface is important in terms of triboelectric respond. Energy generated by triboelectric effect in based on area of fibers. As smother surface of produced fibers will be as much energy be generated.

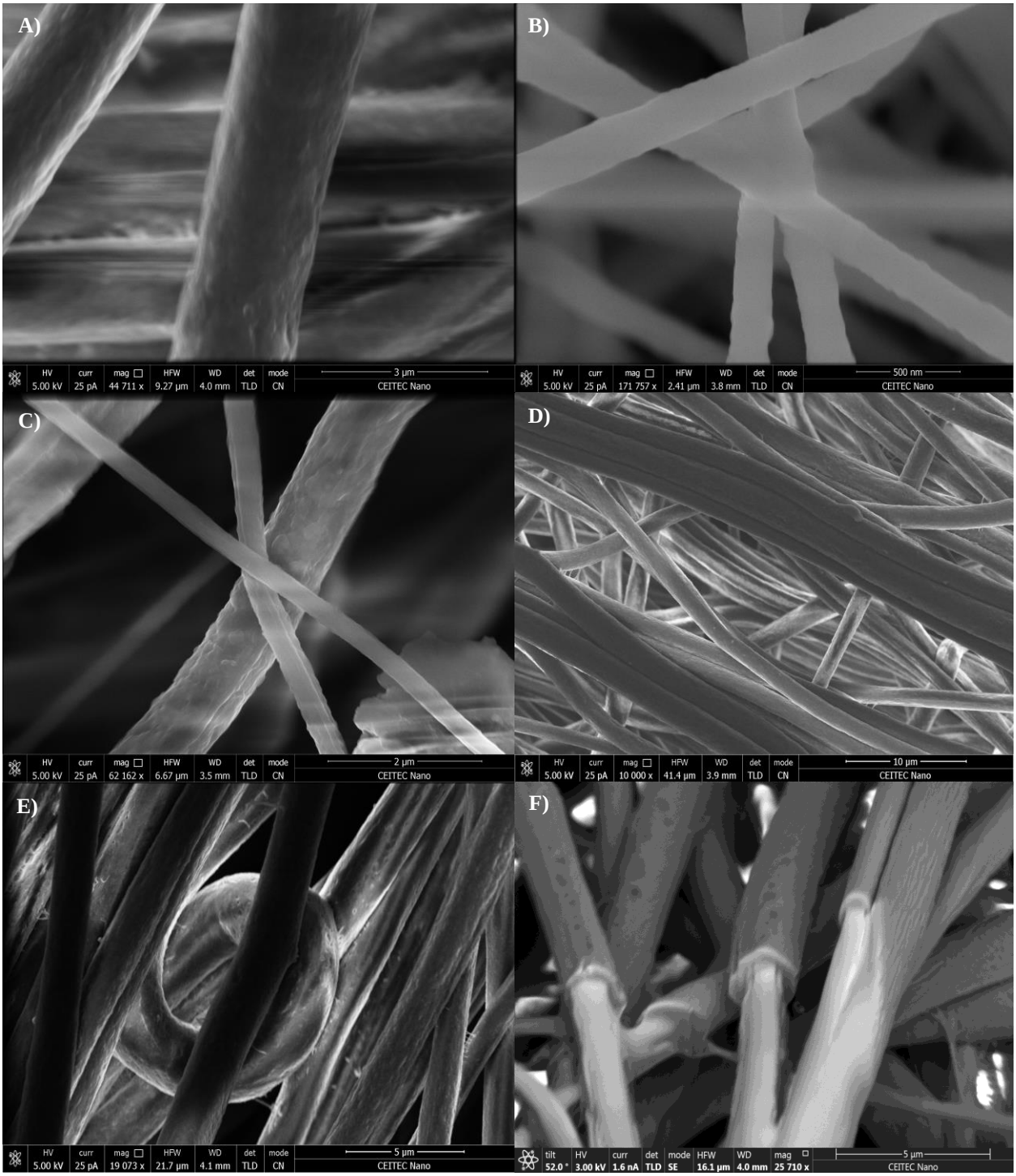


Figure 28. A,B,C,D,E,F) SEM images of produced by electrospinning PVDF samples with humidity percentage: 29–1,2 30−>15% (A); 29–3 30−>20% (B); 29–4 >30% (C); 29–5 30−>15% (D); 29–6 30−>15% (E); 29–7,8 30−>15% (F)

Chapter 4 Experimental section

4.1 Raman Spectroscopy

Raman spectroscopy is popular analytical and research method [33] use spectrum of vibration which provides information about state of extracted molecules of studied material [34]. Raman spectroscopy is non–destructive imaging technique using analysis [35] of rather weak laser light scattered from subjected to illumination by a monochromatic source of photons and providing information about molecular–level [37] composition and molecular structure of the sample. Raman shift [34] which will accrue due to interaction of photons with studied material, also related to molecular bonds vibration. Raman spectroscopy use spectrum of vibration. Spectrum of vibration provide information about state of extracted molecules of studied material. [34] As a result of Raman spectroscopy is continues Spectrum of intensity depends on varieties of Wavenumbers (Raman shift [34]) with certain picks. Wavenumbers also known as Raman shifts or Raman frequencies. Single picks are representing phases of PVDF [36]. Raman spectroscopy allows easily manipulate with smaller samples. [33]

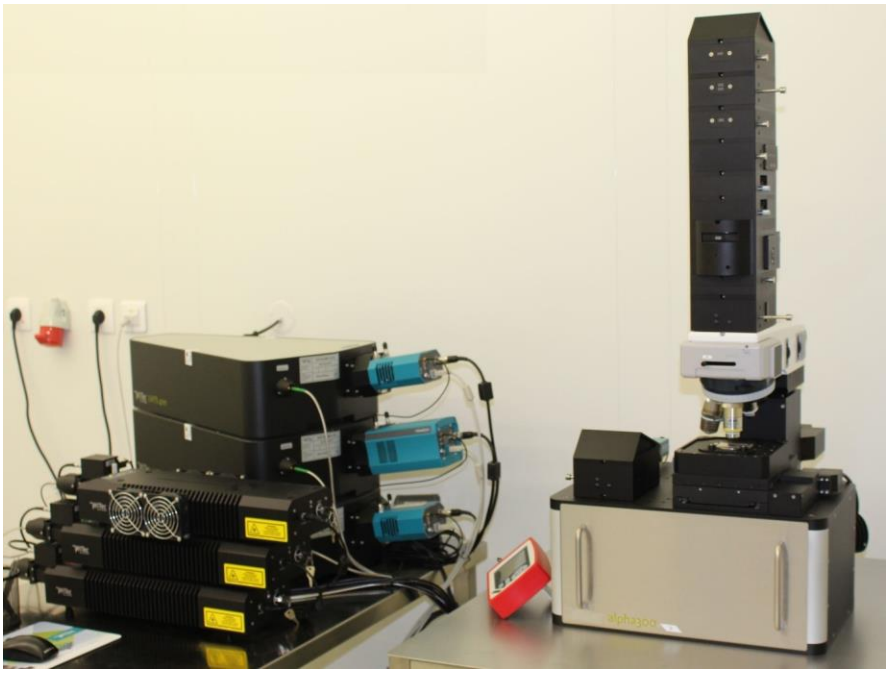


Figure 29. Raman spectroscopy system located on CEITEC Nano [37]

Main disadvantage of the Raman spectroscopy in compare to Fourier–transform infrared spectroscopy is that Raman spectroscopy will not indicate the amount of each phases within the sample but only identify phases.

The method has been proven useful to confirm results of Fourier–transform infrared spectroscopy by easily identified phases of PVDF.

4.2 X–ray Photoelectron Spectroscopy

XPS stands for X–ray photoelectron spectroscopy [38]. X-ray imaging spectroscopy has enabled high resolution studies of the structure of X-ray sources [38]. The technique is used to determent elemental composition, chemical and electronic state of elements that is within a sample. The technique allowed to study wide range of materials from metals, oxides, semiconductors, composite non−organic materials, and biomaterials. The measurement is being carry out on the surface of material within the range of 1 to 10 nm. [39]

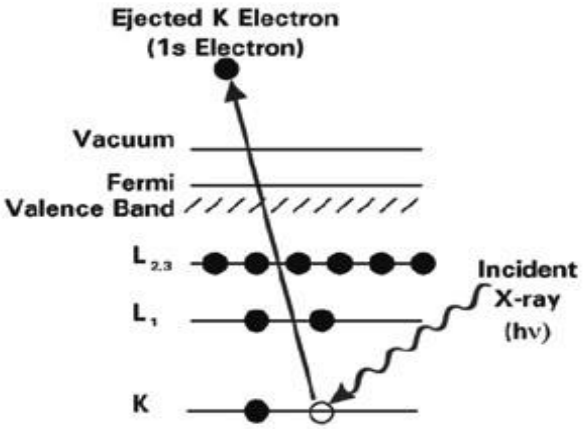


Figure 30. Photoelectric effect [40]

The physical principle of XPS is based on Photoelectric effect in which X–rays are used photon source. As a photon source usually Mg and Al Kα with energy 1256 eV and 1486 eV respectively are used. When X–rays photons interact with a sample electron are extracted from the sample. Kinetic energy of extracted electrons is based on extraction energy of phonons and binding energy of electrons. It is possible to determent unknown element base on this kinetic energy of emitted electrons. XPS detector is also sensitive on chemical environment, wherefore it is capable to determent composite materials from the surface of the sample. [39]

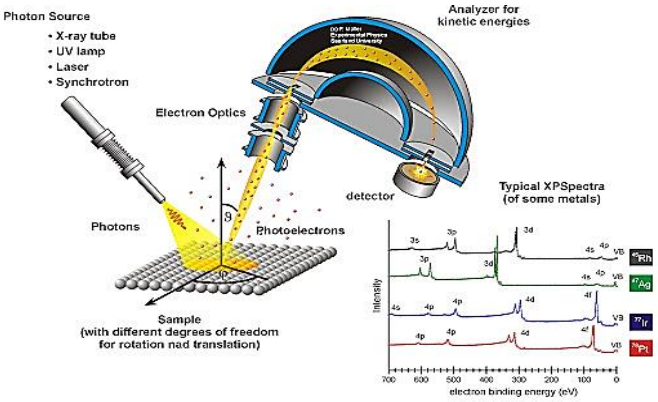


Figure 31. XPS detector [41]

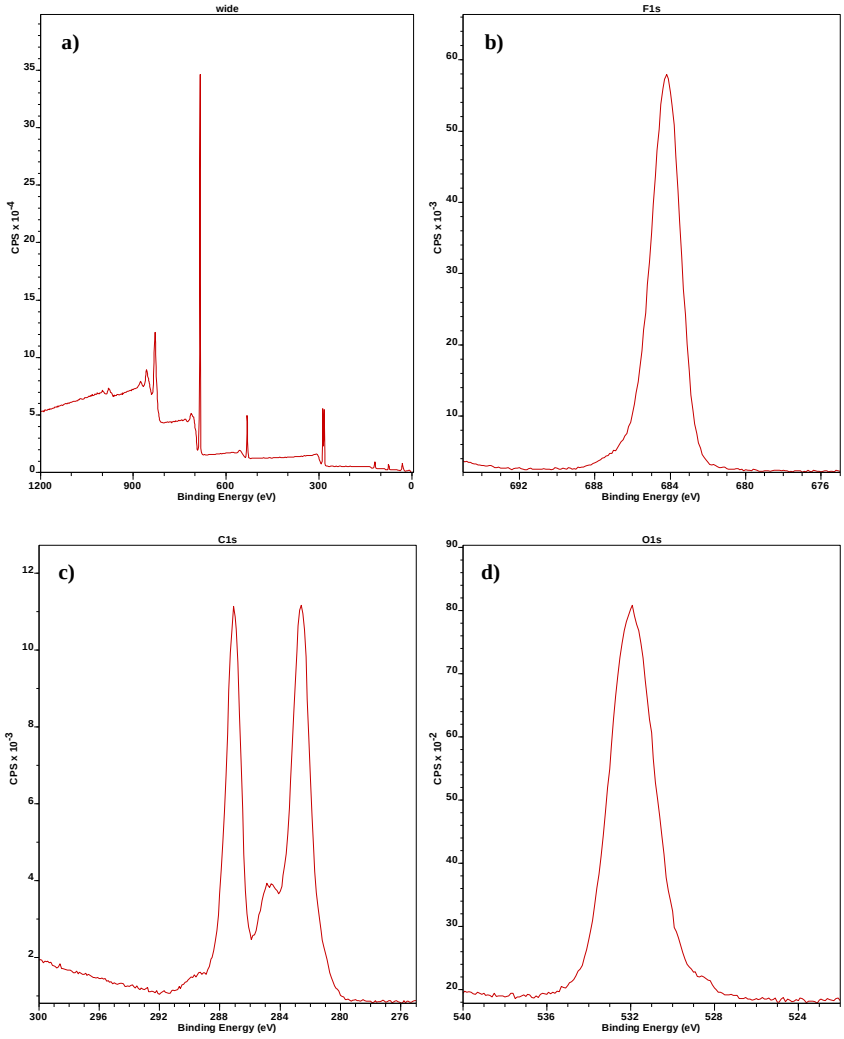


Figure 32. a,b,c,d) XPS spectrum of pure PVDF

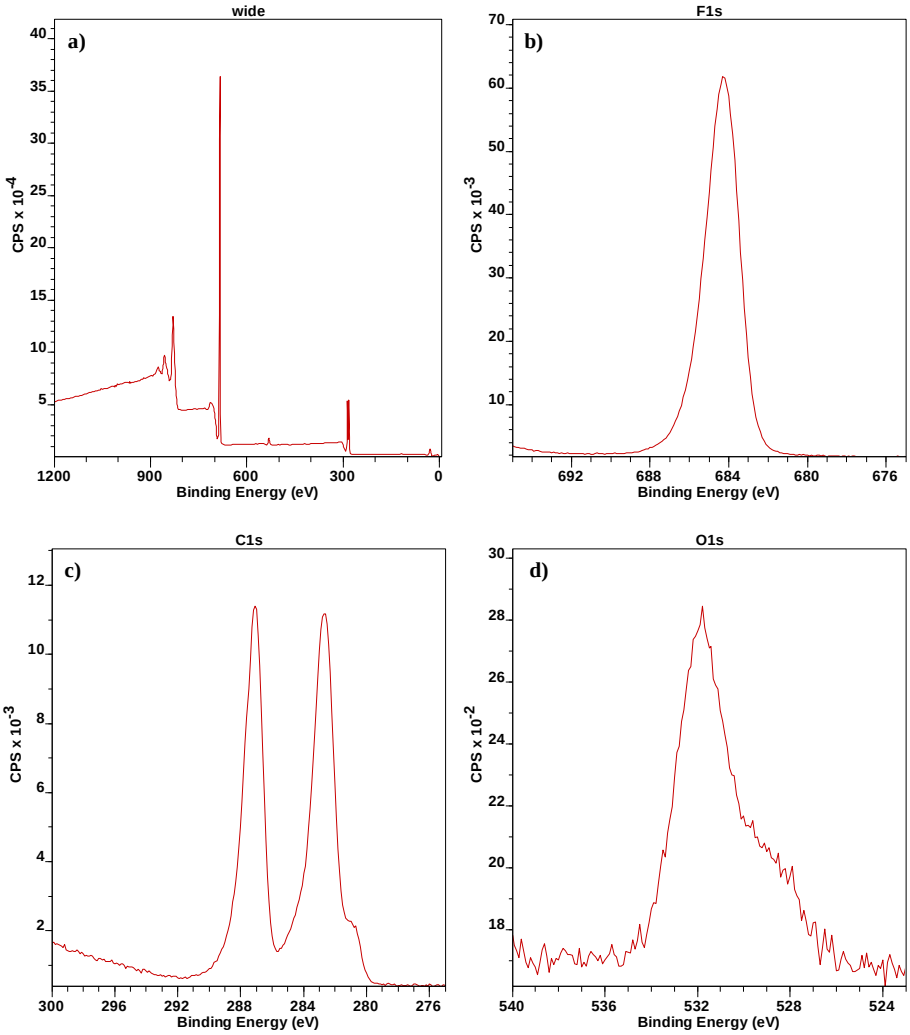


Figure 33. a,b,c,d) XPS spectrum of PVDF−CNT composite

4.3 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared spectroscopy (FTIR) is a technique which analyzing the physical properties of solid, liquid and gas phases. The method is allowed to study absorption and emission properties of materials, identify materials composition. The main principle of the FTIR spectroscopy is based on the absorption of light within infrared spectrum [42]. The main advantage of the method is based on fact what different materials absorb or scattered light differently [43]. The materials can be identified by finding existent spectrum of material in database of Spectrum. The FTIR also provide information about element concentration and amount of phases in the studied material [44].

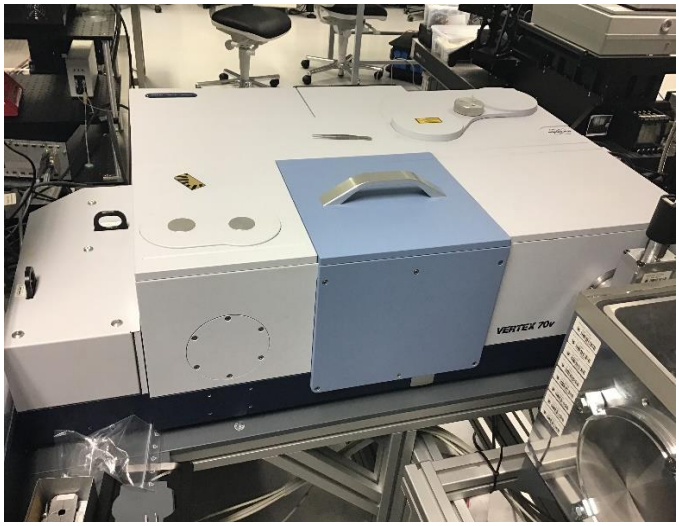


Figure 34. VERTEX 70v system located on CEITEC Nano

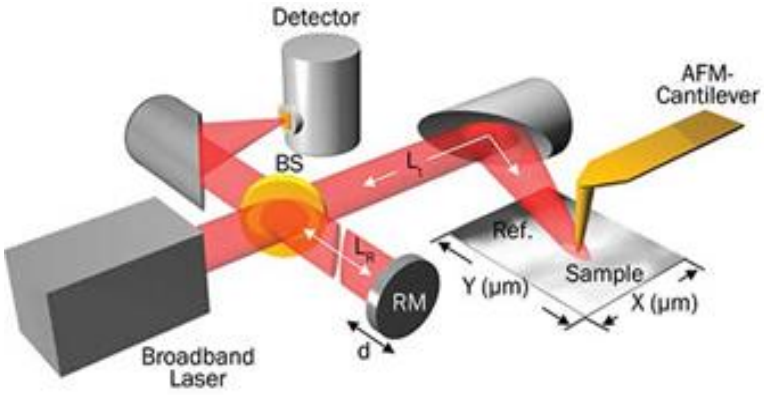
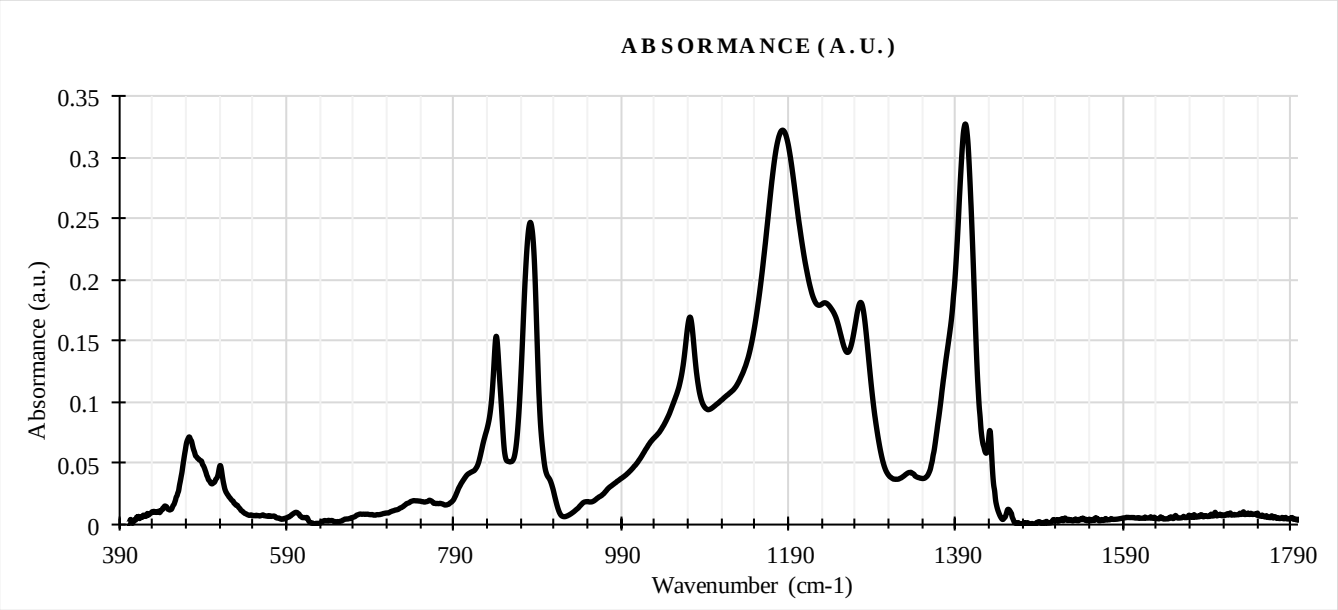


Figure 35. Optic system of FTIR [45]

Before performing the analysis, vacuum must be created in the main chamber to eliminate traces of H_2O or CO_2. The analysis could be done within wide range of infrared region. The device

processing measured signal into output infrared spectrum with Fourier transformation. The analysis can be performed in two modes: transmittance or reflectance. The result of analysis is Spectrum of intensities depend on wavenumbers. The results are different by performing different analysis besides using same sample for both methods. The difference in data between absorbance and reflectance method can be caused by light scattering at rough surface topography. To process data the mathematical method calls Fourier Transformation needs to be applied. Fourier Transformation allows abstain certain pic of wavenumbers. Using these peaks, the concentration of certain material (or its phase) within sample can be obtained.



Graphic 1. FTIR spectrum of Pure PVDF, sample 20–20

4.4 Focused Ion Beam

The Focused Ion Beam (FIB) technology offers a huge opportunity to study nano dimensional structures by using direct nanoscale and micro scale removal of studied material. FIB system combines both study of material cross section and imaging capabilities with high resolution. [46]

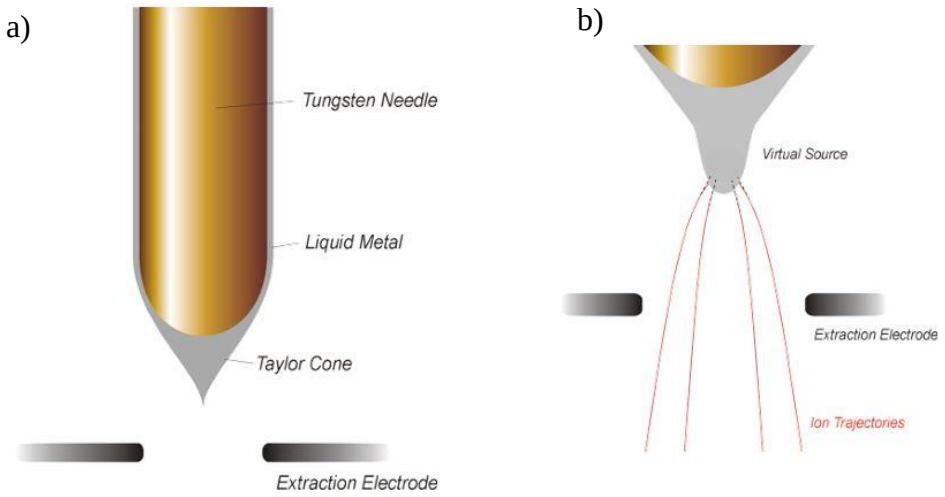


Figure 36. a,b) Taylor cone of liquid Gallium, extraction of ions [47]

Figure 37. Helios FIB system located on CEITEC Nano

The beam is produced from liquid–metal ion sources (LMIS), where ions are formed and extracted by electrodes from Taylor cone. Extracted ion are formed into focused, high−energy

stream of ionized atoms. Grater mass and energy of ions allow them easily to interact with surface of material and extract secondary electrons, allowing ions imaging the sample. During FIB−specimen interaction the sample suffering not only from thermal distraction cause by ions but also accumulating charge carried by ions.

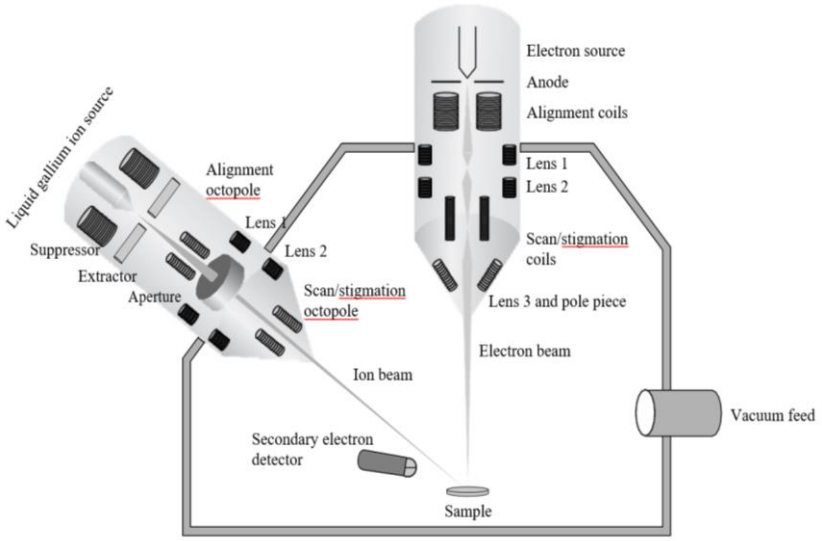


Figure 38. Main chamber of Helios [48]

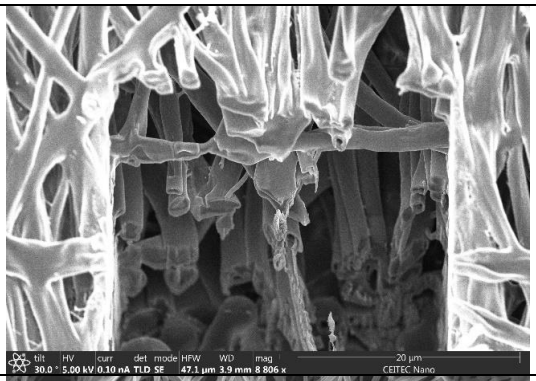
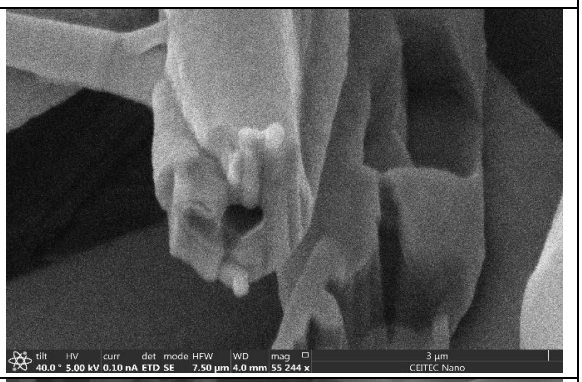
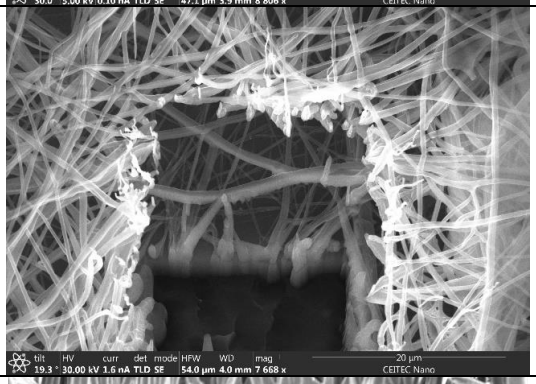
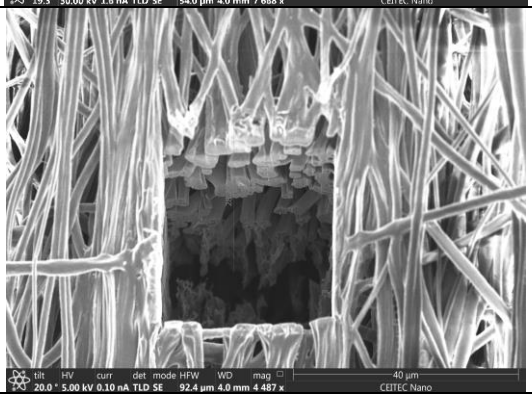
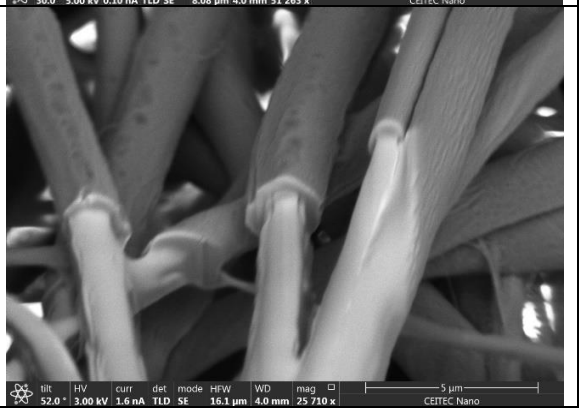
Sample №	Thickness (μm)	Cross–Section image	Milling image
29–1,2	30–32		
29–4	30		
29–5	28		
29–7,8	–	Unavailable due to Brocken aperture	

Table 3. Summarization of FIB process samples

4.5 Measurement of electronic respond

Measurement of electronic respond has been done using experimental system there sample of PVDF material is located between 2 primal electrodes. The primal electrodes are located between secondary electrodes in generator. The generator generates signal of certain frequency and also, measurements mechanical pressure which secondary electrodes apply on PVDF sample. In order to evaluate every samples evenly, every sample has been measurement under same conditions which has been summarized in the table below.

Figure 39. Experimental system

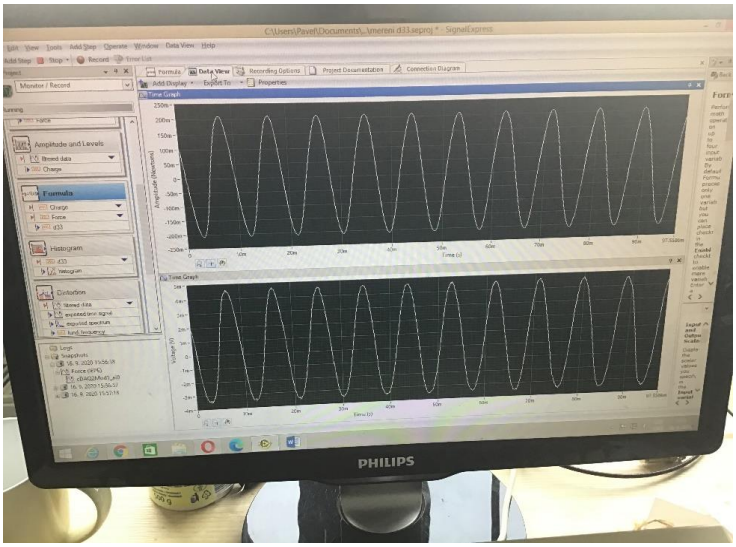


Figure 40. Generated electrical signal of generator and PVDF sample

Sample №	Parameters	Electric respond (μC/N)
29–1,2	Force 500 mN Charge 8 mC	19.3
29–3		4.12
29–4		≈ 2
29–5		10.39
29–6		10.3
29–7,8		6.6

Table 4. Measurement of electric respond

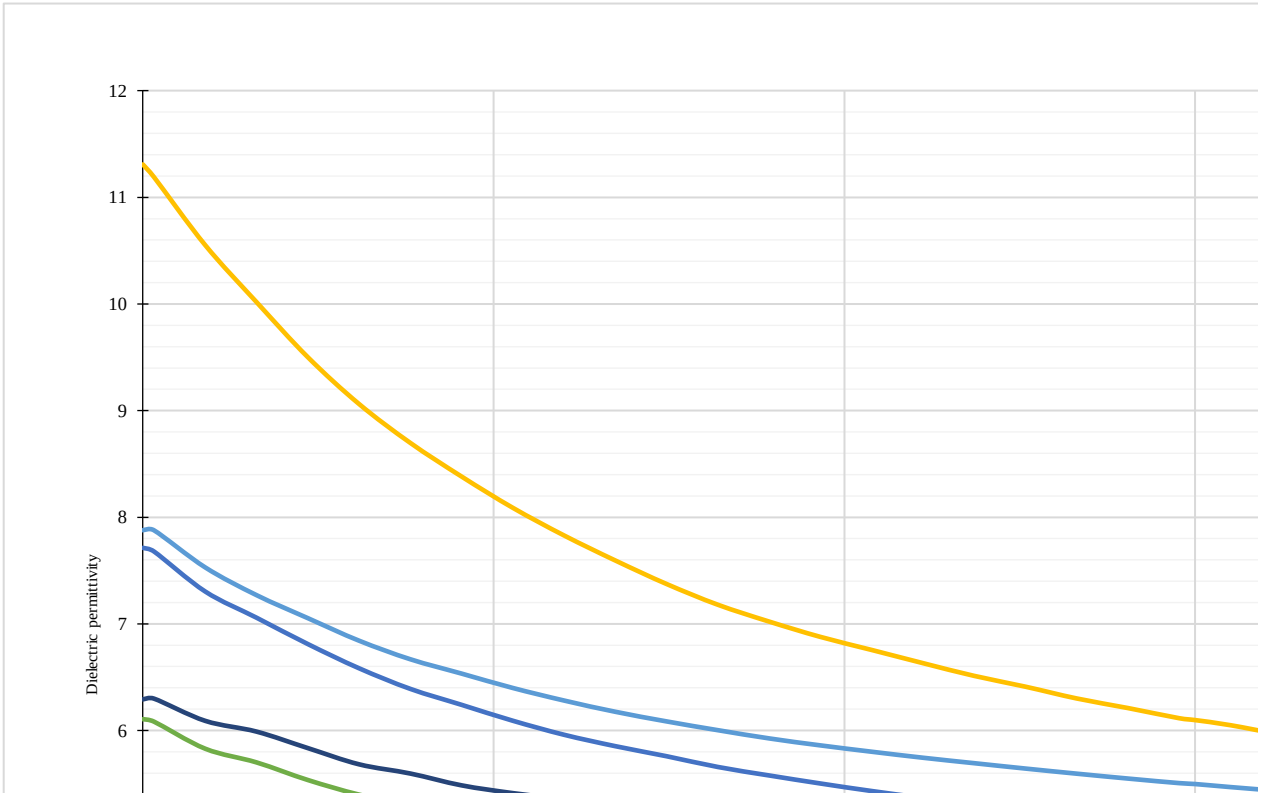
4.6 Measurement of dielectric constant

Permittivity of a material it is ability to store electrical charge when material is exposed to electrical field [49]. One of the most important aspects which represent dielectric properties is dielectric constant.

The dielectric constant was measured by a Novocontrol Alpha Analyzer device. The dielectric constant has been measured in range of 1 Hz to 100 kHz [50].

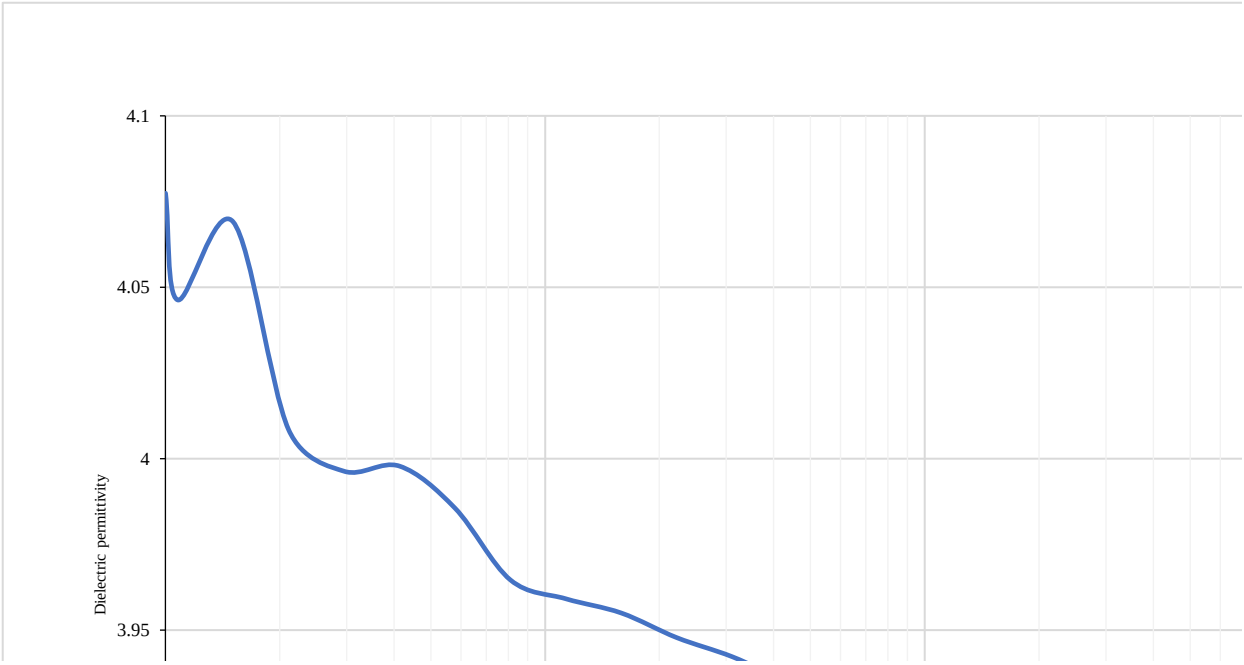
The constant stays high in a area of lower frequency and getting slightly lower in higher [50].

By using device Novocontrol Alpha Analyzer also has been measured conductivity of pure PVDF sample vs PVDF–CNT composite.



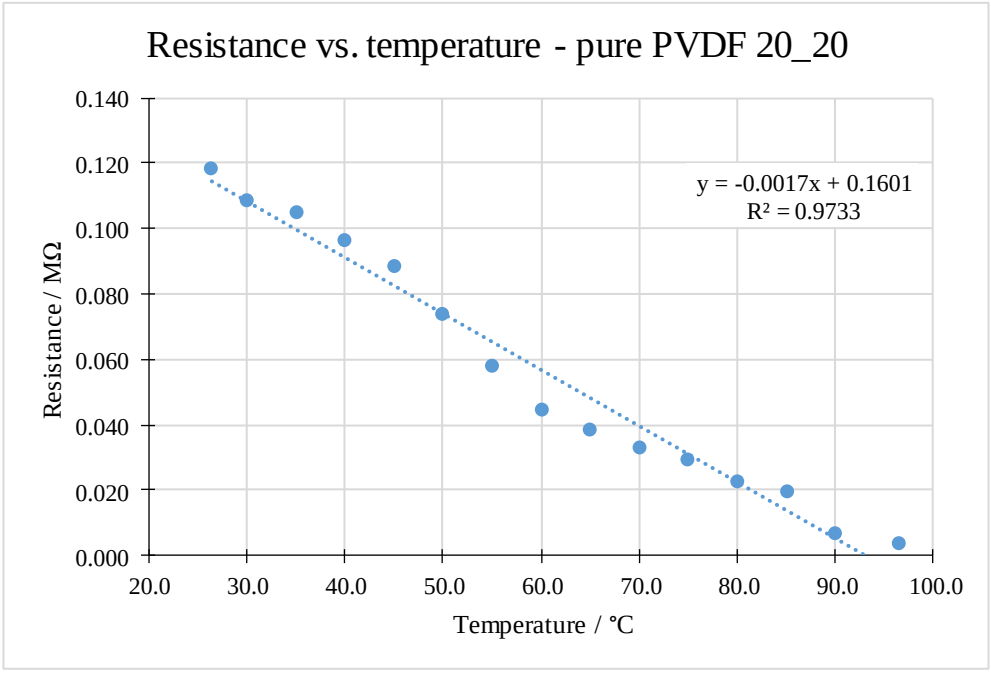
Graphic 2. Measurement of dielectric constant vs frequence, sample 28–5

Overall permittivity of the sample 28–5 is 4.714 (–).

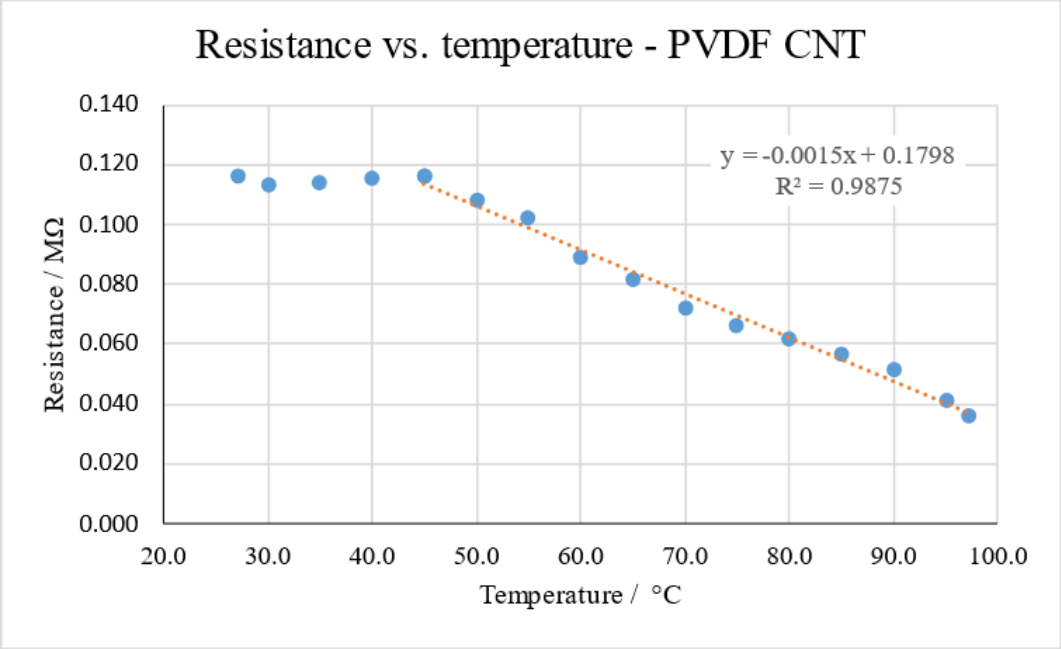


Graphic 3. Measurement of dielectric constant vs frequence, PVDF–CNT composite

Overall permittivity of the sample PVDF–CNT composite is 3.986 (–).



Graphic 4. Dependency of conductivity vs temperature Sample 20–20



Graphic 5. Dependency of conductivity vs temperature PVDF–CNT composite

It has been proven what adding CNT into pure PVDF material improve temperature stability of the composite compound compared to pure PVDF material (Graphic 4,5).

Chapter 5 Future Perspective

It has been found that certain samples produce by same parameters has sings of hollows inside of fibers which give us a ground to try to produce coaxial fibers using CNT. However, there are still unknowns and speculations about mechanism of their formation which require further studding and running more experiments.

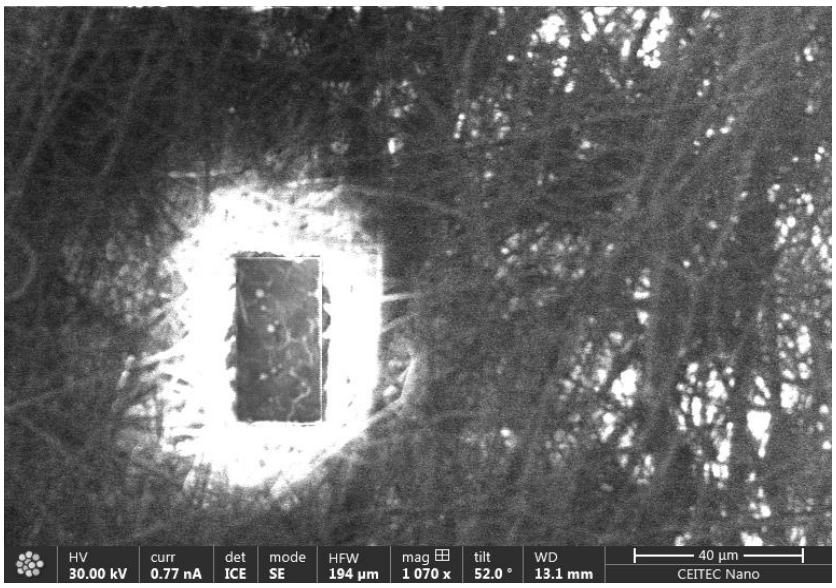


Figure 41. Area of influence of focused ion beam

Figure 42 indicates the area which has been affected by Focused Ion beam. Aggressivity and destructiveness the Gallium FIB do most damage to the sample. Overall damage to the sample makes it hard to properly evaluate morphology. Possible solution which would makes dramatic difference in terms of correct evaluation of morphology produced samples would be using Neon FIB with help of liquid nitrogen cooling. Neon FIB is considered being low energy FIB which has ability to cut single fiber. Liquid nitrogen allows to cool down sample in order to drop destructiveness of FIB.

Chapter 6 Conclusion

The Polyvinylidene Fluoride polymer it is unique materiel, which drown huge amount of attention in nowadays. Even though many aspects of the polymer have been studied good enough, there are still much more that need to be studied further, because the Polyvinylidene Fluoride still did not yet reveal his full potential.

The material has found his place in many areas we all familiar with such as solar panels, batteries, alarm systems, medical masks, filters etc. however, the material has more to offer to all aspects of applied science, manufacture, and medicine.

This study is covered the most popular properties of the polymer main applications the material is used in, characterization of 3 most popular phases the material can crystallize into. There has been described main technologies how to obtain Polyvinylidene Fluoride membranes and the most popular technology calls Electrospinning, which is allowed to obtain nano– micro– fibers of wide range of parameters.

The study also describes main aspects of potential addon to the Polyvinylidene Fluoride polymer, which will enhance his unique properties. This addon is calls Carbon Nanotubes. Carbon Nanotube powder is rather expensive to use as an addon to Polyvinylidene Fluoride, however their unique properties such as conductivity, mechanical strength, chemical resistance is worth to use the nanotubes as a potential addon. There has been described basic aspects of commercial methods of producing nanotubes, their advantages, and disadvantages.

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