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Effect of electrospinning conditions on morphology of PVDF fibers

Bachelor Thesis

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Polüvinüülideenfluoriidi morfoloogiat mõjutavad elektroketruse tingimused

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Töö eesmärk on välja selgitada parimad tingimused piesoelektriliste PVDF kiudude saamiseks elektroketrus meetodil. Uurida lahuse ja elektroketruse parameetrite muutumise mõju kiu morfoloogiale ja kiu diameetrile.

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1. Introduction

1.1. Polyvinylidenefluoride (PVDF)

Polyvinylidenefluoride (PVDF) is a fluoropolymer consisting of the monomer unit $CF_2–CH_2$. The Polymer itself is produced by the polymerization of vinylidene diflouride, as shown on Figure 1.

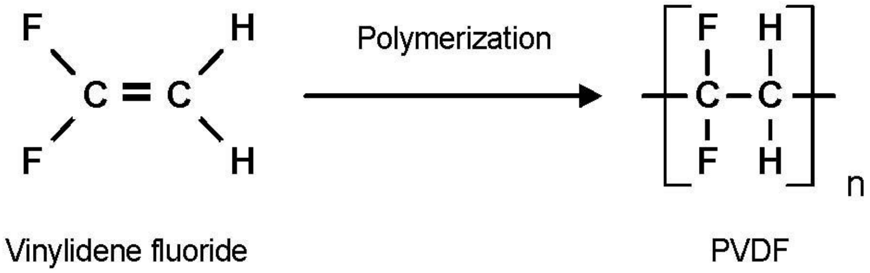
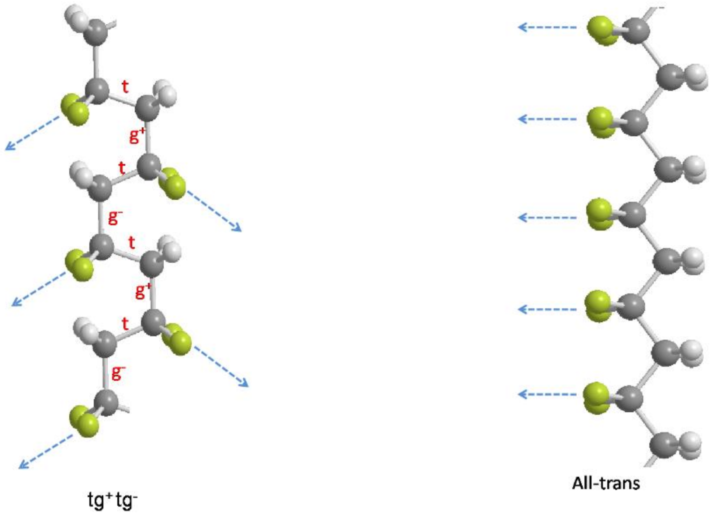


Figure 1. Vinylidene diflouride radical polymerization to Polyvinylidene fluoride [1]

PVDF is a plastic material. It is a high performance polymer. Tensile modulus is from 1.0- 3.0 GPa, which explains the wide usage in piping and cable industry. Generally it is used in applications requiring the highest purity, strength, and resistance to solvents, acids, bases and heat, and low smoke generation during a fire event. PVDF right now is more commonly made into powders, pipe parts, insulators and films. Powders mainly used for enhancing chemical properties of paints to have a better gloss and in lithium-ion batteries. In piping industry it is used due to its chemical stability. It is insoluble in most acids and alkali bases. Insulators could be used in household cables, but mainly in space- and aeronautic materials. Films and membranes are mainly made for high end sensors. Sensing vibration or electrical potential PVDF may be used at temperatures from -62 to 149°C. No oxidation or thermal degradation occurs during continuous exposure to 149°C. Due PVDF-s property of large temperature amplitude, low limited oxygen index of 44% and excellent ultra-violet resistance, it is mainly used in space and aeronautics industry as mentioned before. PVDF has a glass transition temperature (T_g) of about −35 °C and is typically 50–60% crystalline.

Furthermore, it is a polymorphic, semi-crystalline polymer showing at least four crystal phases at different processing conditions [1, 2]. Three chain conformations, corresponding to five crystal phases, have been documented so far: TGTG′ conformation (where T denotes trans and G gauche) for α and δ phases, all trans TTTT conformation for β phase, and TTTGTTTG′ conformation for γ and ε phases. So to better understand what is meant by T trans and G gauche for α and δ phases, a Figure 2 is added.



(a) (b)

Figure 2. (a) TGTG′ and (b) TTTT type of chains of PVDF, where the white and yellow balls represent hydrogen and fluoride atoms. Grey balls represent carbon atoms. Taken from [1].

Both α and β phases are characterized by an orthorhombic unit cell containing two chains. The α phase, the most common polymorph of PVDF, has the conformation with the lowest potential energy. With a nonpolar orthorhombic unit cell, because of anti-parallel packing of the two chains, the α phase is normally obtained by crystallization from the melt at moderate or high undercooling.

Currently, the most important PVDF polymorph is the β phase having a net crystalline dipole moment, oriented essentially in the direction normal to that of the molecular chain, which is responsible for the enhanced piezoelectric and ferroelectric activities [3]. A piezoelectric material responds to mechanical strain and electrical signals. Accordingly, mechanical strain in a piezoelectric material sends an electrical signal or applying voltage creates a mechanical strain. This application is mainly now used in the shape of films. β- phase has mainly been induced in films by mechanically stretching cast molded PVDF to 300% from their original length. This film is then poled by using high voltage to align the dipoles of hydrogen and fluoride. Films are easy to manufacture and inexpensive, however, compared to fiber reinforced composites, they lack a structural ability to be transformed; therefore it limits some potential applications.

The production of PVDF fibers is primarily done by traditional textile methods. These fibers are produced in 10-100 micrometers in diameter, but more desirable fibers are actually in nanoscale range. It has been found that properties of the fiber improve with decreased diameter. This scale provides a structure that has high surface to volume ratio. That means that small concentrations of nanometer sized fibers would have the potential to greatly modify composite properties with possibility to incorporate into aircraft and automobile manufacture. These properties are being used also in the medical field. PVDF nano-scale can be used in novel sensors. These electrospun nanofiber webs can be stacked on each other, creating a good flexible sensor that could monitor static and dynamic pressure which could be used for measure walking speed, because muscles create strains and pressure on the sensor, therefore it can be registered as an electrical signal.

Another application of PVDF is in batteries. PVDF powder is used to design proper electrodes in Lithium-ion rechargeable batteries. PVDF acts as a binder and it is used together with a conductive additive. The interaction between the polymer and conductive additive changes proportionally to particle surface area. The PVDF binder interaction with conductively active material on the micro or nano scale enhances the performance in a Lithium-ion battery.

Nano-scale fibers though are used as separators in lithium-ion batteries. PVDF nanofiber based membranes have been extensively studied for making separators due to its excellent chemical resistance, high mechanical strength, good thermal stability, and high affinity to electrolyte solution. These properties provide high electrolyte uptake and facile transports of ions in a battery, which in turn creates a high performance battery.

Although PVDF fibers were used mainly as separators in batteries, these fibers can be also used as generators. For example harvesting energy from body motion or human activity has a strong potential, which can untie modern personal life from the messy connections of wires for electric power supply. According to such a concept, nanowire based nano-generators built on textile fibers or solid substrates have been demonstrated for the harvesting of mechanical energy produced by the friction-motion of two fibers or ultrasonic waves [14, 15]. Therefore these fibers that were formed in this experimental thesis could be used to produce membranes or yarns that can be woven. So, these membranes or woven textiles could be used for harvesting electrical energy from mechanical energy.

Among the different methods used for production nano-scale fibers like electrospinning, template synthesis, phase separation and self-assembly, the most promising is the electrospinning technique due to its many advantages such as low cost, simplicity of process, repeatability, control of fiber morphology and dimension, etc. In situ induction of polar phase and the spontaneous dipolar orientation of electro-active polymers by a single-step electrospinning process eliminates the need for direct-contact or corona-filed poling resulting in an arc-free processing. During electrospinning process the large draw ratio and draw rate is used. This results in aligning of the polymeric chains along the fiber axis which can lead to favorable β-crystalline phase. As it is known for PVDF, its film shows a predominantly non-polar α-phase without any post-processing treatment. However, the electrospinning process is found to induce the polar β- phase [18] and there is no need in post-processing treatment.

1.2. Electrospinning

Electrospinning process was already patented in 1934 Formhals, where an experimental setup was outlined for the production of polymer filaments using electrostatic force [5]. Today it is a broadly used technology for electrostatic fiber formation which utilizes electrical forces to produce polymer fibers with diameters ranging from 2 nm to several micrometers using polymer solutions of both natural and synthetic polymers [6]. The electrospinning process, in its simplest form consists of a pipette to hold the polymer solution, two electrodes and a direct current (DC) voltage supply in the kV range. Although electrospinning is a pretty simple process, requiring just simple laboratory equipment to yield fibers down to the nano-scale, the science behind it is not simple at all. Electrospinning process involves the understanding of electrostatics, fluid rheology and polymer solution properties such as rate of solvent evaporation, surface tension and solution conductivity. These fundamental properties are constantly interacting and influencing each other during the electrospinning process [5].

Important features of electrospinning are: suitable solvent should be available for dissolving the polymer; the vapor pressure of the solvent should be suitable so that it evaporates quickly enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range; the viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the pipette; the power supply should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette; and the gap between the pipette and grounded surface should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to form [5].

When the force exerted by the electric field, formed between the droplet and a grounded collector, overcomes the surface tension, a thin jet is formed. The jet of the charged solution is accelerated towards the collector under the action of the electric field. If the concentration of the solution is sufficiently high (viscous) to stabilize the jet, the polymer solution is severely stretched and the solvent evaporates to form ultrathin fibers which solidify and are deposited on the collector forming a non-woven mesh of fibers [16].

1.1.2. Effects of Various Parameters on Electrospinning

The parameters affecting electrospinning and, as a result, the fibers may be broadly classified into solution parameters, ambient parameters, and process parameters. Solution parameters include molecular weight, concentration, conductivity, viscosity, surface tension and dielectric effect of solvent; and process parameters include applied electric field, tip to collector distance, collector types, diameter of needle and feeding or flow rate. Each of these parameters significantly affects the fibers morphology obtained as a result of electrospinning, and by proper manipulation of these parameters one can get nanofibers of desired morphology and diameters [5, 6]. Table 1 shows brief overview about various parameters on electrospinning and their effects on fiber morphology.

Table 1. Electrospinning parameters and their effects on fiber morphology [6]

Parameters	Effect on fiber morphology
Viscosity	Low-beads generation, high-increase in fiber diameter, disappearance of beads.
Polymer concentration	Increase in fiber diameter with increase of concentration.
Molecular weight of polymer	Reduction in the number of beads and droplets with increase of molecular weight.
Conductivity	Decrease in fiber diameter with increase in conductivity.
Surface tension	No conclusive link with fiber morphology, high surface tension results in instability of jets.
Applied voltage	Decrease in fiber diameter with increase in voltage.

Distance between tip and collector	Generation of beads with too small and too large distance, minimum distance required for uniform fibers.
Feed rate	Decrease in fiber diameter with decrease in flow rate, generation of beads with too high flow rate.
Humidity	High humidity results in circular pores on the fibers.
Temperature	Increase in temperature results in decrease in fiber diameter.

Molecular weight is one of the important solution parameters affecting the morphology of electrospun fiber. Too low molecular weight solution tends to form beads rather than fibers and a high molecular weight solution gives fibers with larger average diameters. Molecular weight of the polymer reflects the number of entanglements of polymer chains in a solution, thus solution viscosity.

Chain entanglement plays an important role in the processing of electrospinning. For example, when polymer concentration is low, high molecular weight polymer can maintain enough number of entanglements of the polymer chains, thus ensuring a sufficient level of solution viscosity to produce a uniform jet during electrospinning and restrain effects of surface tension, which plays a significant role in beads formation on electrospun nanofibers. So, high molecular weights are not always essential for the electrospinning process if sufficient intermolecular interactions can provide a substitute for the inter-chain connectivity obtained through chain entanglements [5, 6].

Solution conductivity is mainly determined by the polymer type, solvent used, and the availability of ionisable salts. If the conductivity of the solution is increased, more charges can be carried by the electrospinning jet. With the increase of electrical conductivity of the solution, there is a significant decrease in the diameter of the electrospun nanofibers whereas with low conductivity of the solution, this results in insufficient elongation of a jet by electrical force to produce uniform fiber, and beads may also be observed. Generally, electrospun nanofibers with the smallest fiber diameter can be obtained with the highest electrical conductivity [5, 6].

To initiate electrospinning process the charged solution needs to overcome its **surface tension.** Surface tension has the effect of decreasing the surface area per unit mass of a fluid. In this case, when there is a high concentration of free solvent molecules, there is a greater tendency for the solvent molecules to congregate and adopt a spherical shape due to surface tension. A higher viscosity will mean that there is greater interaction between the solvent and polymer molecules thus when the solution is stretched under the influence of the charges, the solvent molecules will tend to spread over the entangled polymer molecules thus reducing the tendency for the solvent molecules to come together under the influence of surface tension [17].

Effect of voltage and distance in electrospinning is also one of the factors that affect uniformity and beading. At lower distances the flight time of the jet is insufficient for solvent evaporation and clumping (beading) of solvent is found to be present. Vice versa, longer distance improved flight time and allows solvent to evaporate. Voltage needs to be strong enough to create an electric field which will break the surface tension of the solution to initiate electrospinning. Too high voltages produce unstable jet. Jet behaves erratically and flies upward and away from the collector. Every solution has its own suitable distances and voltages. Best characteristics of fibers are always found somewhere in the middle of high and low for both voltages and distances [19].

Type of collector also plays important role in electrospinning. Generally, aluminum foil is used as a collector but due to difficulty in transferring of collected fibers and with the need for aligned fibers for various applications, other collectors such as conductive paper, conductive cloth, wire mesh, pin, parallel or gridded bar, rotating rod, rotating wheel, liquid non solvent such as methanol coagulation bath and others are also common types of collectors nowadays [5, 6]. On the next pictures Figure 2 is an example of a setup which was used in this bachelor thesis as well.

Understanding the basics behind the materials and the fundamentals that affect electrospinning will open new avenues and applications for electrospun fibers. With smaller pores and higher surface area than regular fibers, electrospun fibers have been successfully applied in various fields, such as, nano-catalysis, biomedical, tissue engineering scaffolds, protective clothing, filtration, pharmaceutical, optical electronics, healthcare, biotechnology, defense and security and environmental engineering. Electrospun nanofibers also offer several advantages such as, an extremely high surface-to-volume ratio, tunable porosity, malleability to conform to a wide variety of sizes and shapes and the ability to control the nanofiber composition to achieve the desired results from its properties and functionality [5].

2. Objectives

The aim of the work was to find out the best conditions to produce piezoelectric PVDF fibers by electrospinning and study the effect of solution and electrospinning parameters on morphology and sizes of electrospun fibers.

Experimental tasks:

To study the effect of solution parameters such as:

- Acetone content in binary solvent (from 0 up to 60 vol.%)
- Viscosity of solutions
- Conductivity of solutions
- Surface tension of solutions
- Sonication
- Polymer molar mass (PVDF with two molar masses of 275 and 530 kg/mol were taken for analysis)

and electrospinning parameters as:

- Applied voltage
- Distance to collector

on morphology and sizes of the PVDF fibers

3. Experimental

3.1. Materials

The PVDF with molar masses 275000 g/mol (PVDF-275) and 530000 g/mol (PVDF-530) from Sigma-Aldrich was used. The solvents used were N,N-dimethylformamide (DMF, Merck 99.5%) and acetone (Merck, 99.7%). Fluorosurfactant Capstone FS-66 was purchased from Sigma-Aldrich.

3.2. Solution preparation

Solvents were mixed in different volume ratios v/v DMF/Acetone to be used as a binary solvent for PVDF solutions. Certain amount of PVDF was dissolved in binary solvent of DMF/Acetone and mechanically stirred with magnetic bars at 30-40°C until a transparent and visually homogeneous polymer solution was formed. The solution then was cooled to ambient temperature for electrospinning. Some of solutions were ultrasonically stirred. The 3 wt% of fluorosurfactant to the weight of whole solution was added to several polymer solutions in order to study the effect of surfactant. Solutions were prepared at various polymer concentrations: 16% and 20% for PVDF-530, and 16%, 20%, 25% for PVDF-275 using as solvent pure DMF and 4:1, 1:1 and 2:3 v/v mixture of DMF with acetone. Concentration of polymer in solution was calculated by the formula: $C = \frac{mass\ of\ polymer}{mass\ of (polymer+solvent)} \cdot 100\%$.

3.3. Instrumentation and Characterization

Electrosospinning was done by DC voltage (Glassman high voltage) connected to a syringe which was clipped from the end to help create a better Taylor cone. A 1 ml syringe was placed in a syringe pump (New era pump systems, Inc). Throughout this thesis a pumping rate of 0.7-1.5 ml/h was used. Needle diameter was 0.8 mm. Negative voltage was applied to the needle tip. Fibers where pulled onto a spinning drum. The spinning drum method helps to create a mat of fibers because they are aligned and dry. The setup of a spinning drum and the syringe pump is on Figure 3.

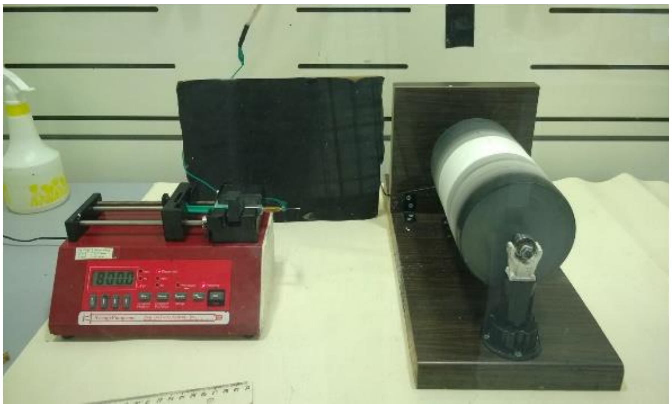


Figure 3. Electrospinning setup with syringe pump and a spinning rotating drum collector

Each of solutions was studied at various voltages (10-20 kV) and distances (10-20 cm) while pumping rate and solution concentration were kept the same.

For ***sonication*** the ultrasonic device Bandelin electronic with horn configuration was used. ***Viscosity*** of solutions was measured at room temperature in a rotating viscometer (Brookfield DV-II + Viscometer).

(a) (b)

Figure 4. (a) Bandelin electconic UW2070 ultrasonicator and (b) Brookfield DV-II + Viscometer

Measurements of ***electric conductivity*** of solutions were done with Metler Toledo conductivity meter. ***Surface tension*** of electrospun PVDF solutions was tested at room temperature by pendant drop method with tensiometer Dataphysics OCA (contact angle system).

A Tabletop scanning electron microscope TM-1000 Hitachi and polarized light microscope Zeiss Axioskop 2 were used to observe the morphology of PVDF fiber mats.

4. Results and Discussion

4.1. Effect of added acetone

The solvent used in polymer solutions for electrospinning is one of the most important parameters determining the possibility of formation and resulting morphology of the electrospun fibers. DMF is a good solvent for dissolution of PVDF. As it is known, DMF shows strong polarity due to its higher electron donating index, dielectric constant, and dipole moment. However, DMF possesses a high boiling temperature, 153.0°C, as can be seen from Table 2.

Table 2. Comparison of solvent properties

Solvent	Electron Donating Index	Dielectric constant	Dipole moment (D)	Boiling point (℃)
Acetone	17.0	20.9	2.84	56.2
DMF	26.6	36.7	3.80	153.0

The polarity of DMF could facilitate the formation of fibers, but the low volatility and high surface tension could make the fiber generation difficult from PVDF in DMF solutions. Indeed, as it can be seen from the Figure 5, it was not possible to electrospin any fibers from

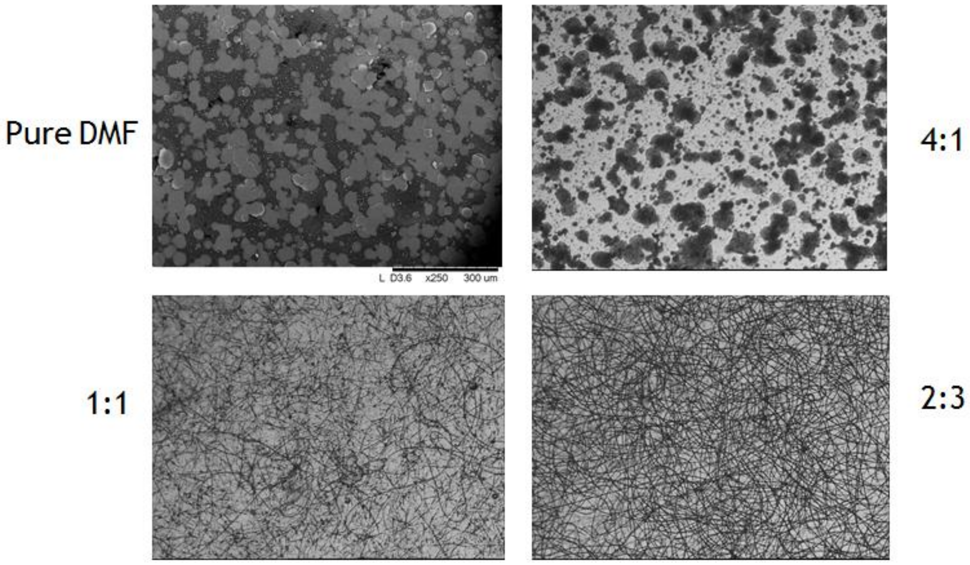


Figure 5. Optical light micrographs of electrospinning of PVDF in DMF/Acetone mixture:
A) Pure DMF, B) PVDF in 4:1 DMF/Acetone, C) PVDF in 1:1 DMF/Acetone, D) PVDF in 2:3 DMF/Acetone. Voltage 15 kV, distance 15 cm, pumping rate 0.7 ml/h

the solution of PVDF in pure DMF, and only droplets of solutions were observed. Taking into account the higher volatility of acetone, which has a lower boiling temperature of 56.2°C (see Table 2), it is expected that addition of acetone can promote the electrospinning of PVDF in a mixture of DMF and acetone. As can be seen from the figure 5, addition of small amount of acetone to DMF, namely 4:1 ratio of DMF/Acetone, still does not stimulate the generation of fibers. However, further increase in acetone content helped to achieve rather stable electrospinning process with formation of fibers.

As it is known, the initiation of electrospinning also requires the charged solution to overcome its surface tension. Figure 6 presents the influence of added acetone on surface tension of solutions of PVDF-530 in DMF/Acetone. The higher the acetone content (lower DMF weight fraction), the lower is the surface tension of solution that helps the charged solution to overcome the surface forces. Therefore, the initiation of electrospinning of fibers from solutions with high enough acetone content can be explained by both higher volatility of binary solvent and lower surface tension of solutions.

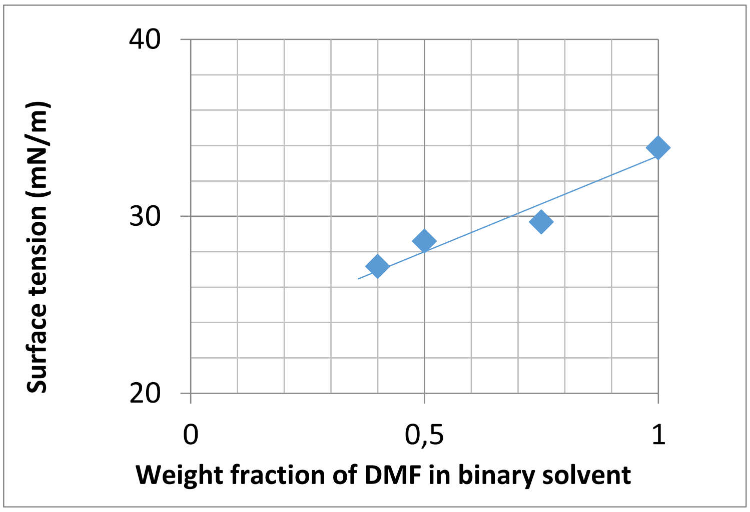


Figure 6. Effect of added acetone on surface tension of PVDF-530 solution. Concentration of solution was kept the same 16%.

The scanning electron micrographs in Figure 7 present the morphology of the fibers electrospun from PVDF-530 in 1:1 and 2:3 DMF/Acetone. For both solvents ratios the fiber mats characterized by nanofibers with typical beads-on-string morphology with a cylindrical fiber structure. At lower acetone content fibers are more homogeneous in diameters. At higher acetone content, more beaded fibers can be produced. The similar results for PVDF nanofibers prepared from DMAc/Acetone solutions were reported in [19], where they found an increase of the population and size of beads with an increase in the acetone fraction in the solution.

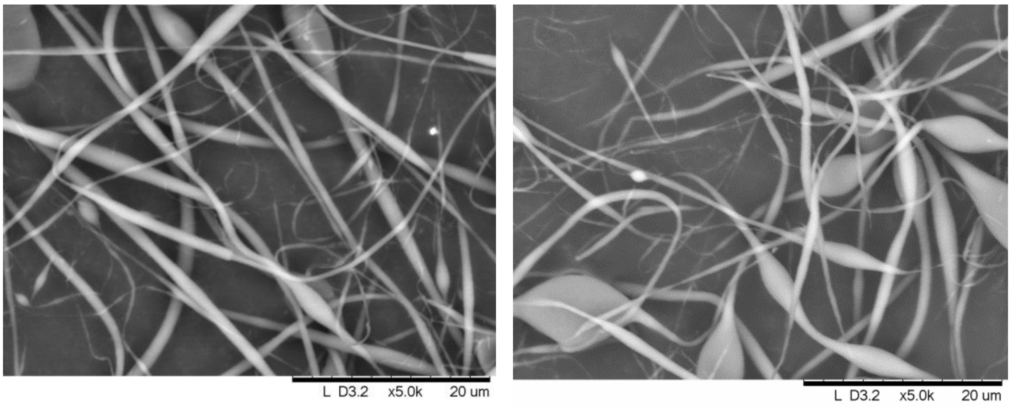


Figure 7. Micrographs of the fibers electrospun from PVDF in 1:1 (a) and 2:3 DMF/Acetone (b). Distance 20 cm, voltage 20 kV, pumping rate 1 ml/h.

In the electrospinning process a crucial element affecting the fiber morphology is the applied voltage and distance between needle tip and collector. Therefore, samples of PVDF-530 and PVDF -275 were collected at various distances (10 cm and 20 cm), and voltages (10, 15 and 20 kilovolts). In most cases, a higher voltage causes greater stretching of the solution due to the greater columbic forces in the jet as well as a stronger electric field and these effects lead to reduction in the fiber diameter, bead sizes and also rapid evaporation of solvent from the fibers. Therefore, all the solutions were studied at various voltages from 10 kV up to 20 kV. Figure 8 shows as example the morphology of electrospun fiber mats produced from solution of PVDF-530 in 2:3 DMF:Acetone.

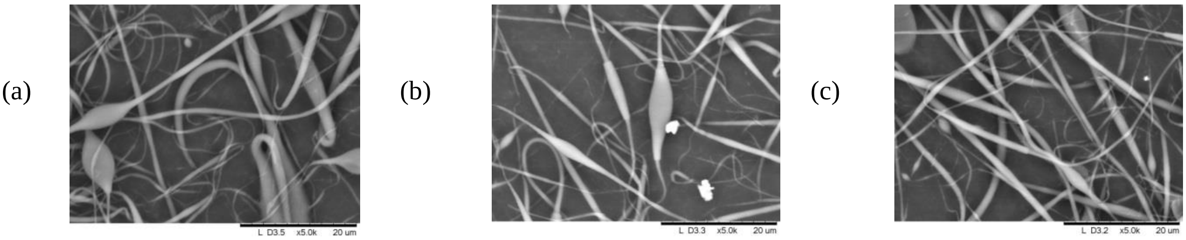


Figure 8. Effect of applied voltage on morphology of PVDF-530 fibers. Distance was kept the same 20 cm, pumping rate 1 ml/h. Solution concentration is 16%. Voltage applied: (a) 10 kV; (b) 15 kV; (c) 20 kV.

As seen, morphology of fibers does not change with applied voltage in the range of 10-20 kV, and still beaded fibers are observed. Average diameters of the fibers at different voltages were calculated and are shown in Figure 9.

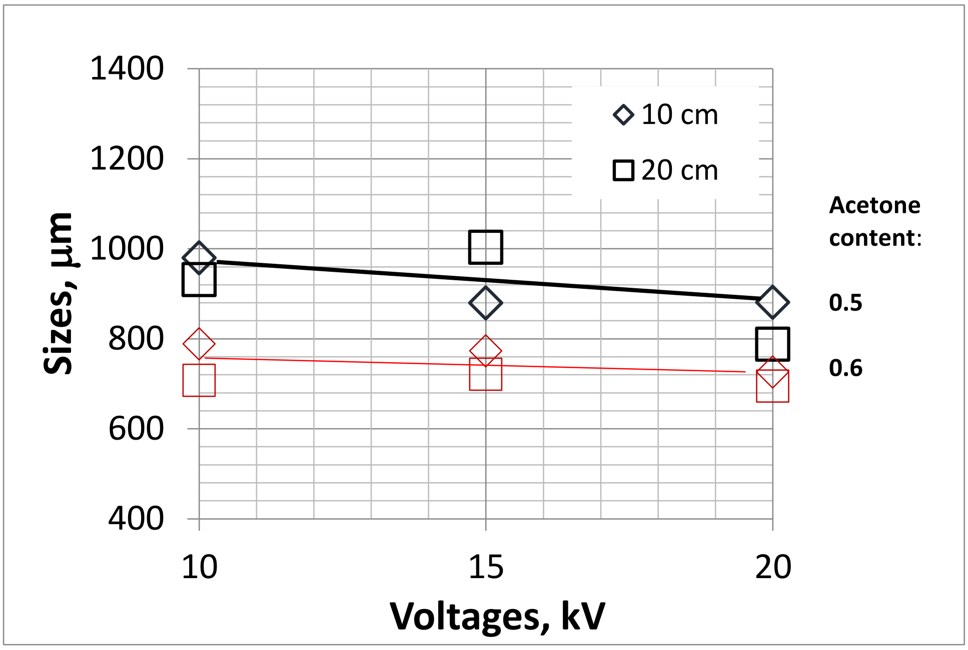


Figure 9. PVDF-530 16% DMF/Acetone 1:1 and 2:3 average diameters of fibers depending on the voltage, distance and acetone content

As can be seen from the figure, there is only very slight (or even no) dependence of diameters on applied voltage.

Varying the distance between the needle tip and collector affects the electric field and also the flight time of the jet. Theoretically, at smaller distances the jet has a smaller flight time to travel to the collector and the stronger electric field increases the acceleration of the jet. As a result larger fibers should appear. However, in this work it was found that used distance to collector does not affect the diameters of the PVDF fibers (see Figure 9): all these samples were found to have similar averaged diameters at different used distances that are within experimental error of each other.

At the same time, added acetone shows the great influence on fiber diameters, and the higher the acetone content in binary solvent, the smaller are the diameters of fibers. Such an effect can be attributed to the difference in viscosity of solutions. Viscosity data are shown in Figure 10 as a function of DMF content in 16% PVDF-530 solutions for several mixed solvent systems. As can be seen from the Figure 10, with increasing acetone content, viscosity of polymer solutions decreases drastically, and viscosity shows a good linear relationship with respect to the DMF content in the mixed-solvent systems. Probably, acetone being a non-solvent of PVDF reduces the hydrodynamic radius of the polymer in solution, leading to lower viscosity. Lower viscosity, from the one side, leads to generation of fibers having smaller sizes that is observed in Figure 9. However, from another side, lower viscosity causes fewer molecular entanglements between PVDF chains and promotes beaded fibers as confirmed by Figure 7.

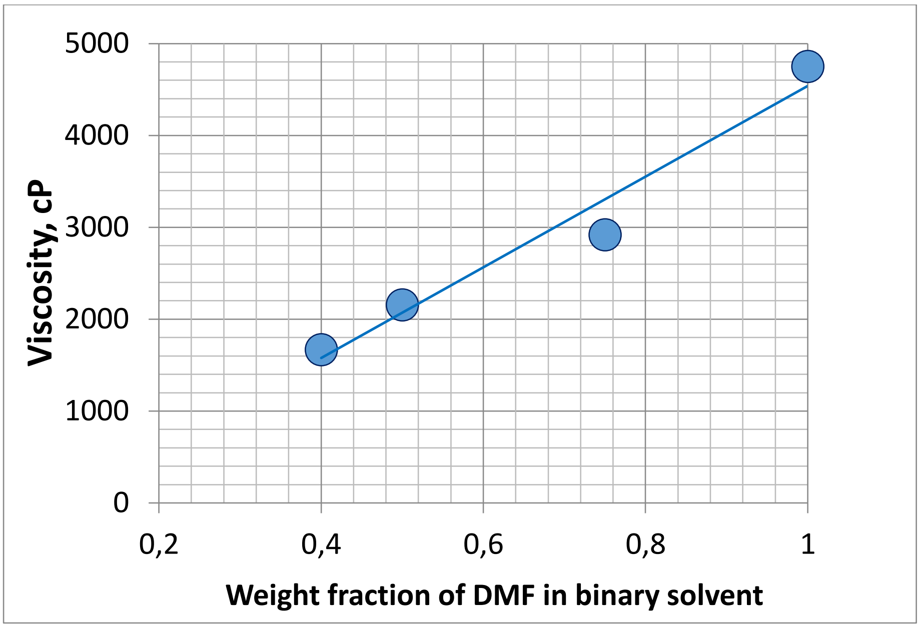


Figure 10. Viscosity dependence of DMF in binary solvent with acetone

Transitions from electrospraying of droplets to spinning of beaded fibers, and finally to spinning of uniform fibers have often been reported in the literature. Recently, attempts have been made to explain such transitions in terms of inter-chain contacts. The critical concentration for chain overlap is C*=1/[η], where [η] is the polymer intrinsic viscosity. Depending on the polymer molecular weight distribution, Gupta *et. al.* [20] found that C/C*≥10 gave uniform fibers for polydisperse polymer.

Intrinsic viscosity of PVDF-530 in DMF was measured (by Dr. E. Tarasova) and was 0.55 dl/g. Consequently, C*= 1.8%, so 16%-solution corresponds to C/C*= 8.8. This can be the reason of beaded fibers obtained at concentration 16%. Therefore, the solution with higher PVDF-530 concentration, namely 20%, was studied. In this case, estimated C/C*= 11.1 which is higher than 10. Figure 11 shows as example the SEM micrographs of fibers electrospun from solutions of PVDF-530 in 1:1 DMF/Acetone with concentrations of 20% and 16% for comparison.

Concentration seems to have the most effect on viscosity and morphology of the fibers. 20% fibers are on average much thicker than 16% fibers. For example, at the same distance of 20 cm and the same voltage of 20 kV, 20% fibers have average diameter of 950 nm in contrast to 780 nm for 16% fibers. Higher viscosity results in disappearing of beads. However, 20% solution forms wetter fibers causing the fibers to mesh together as clearly seen from Figure 10(b*).

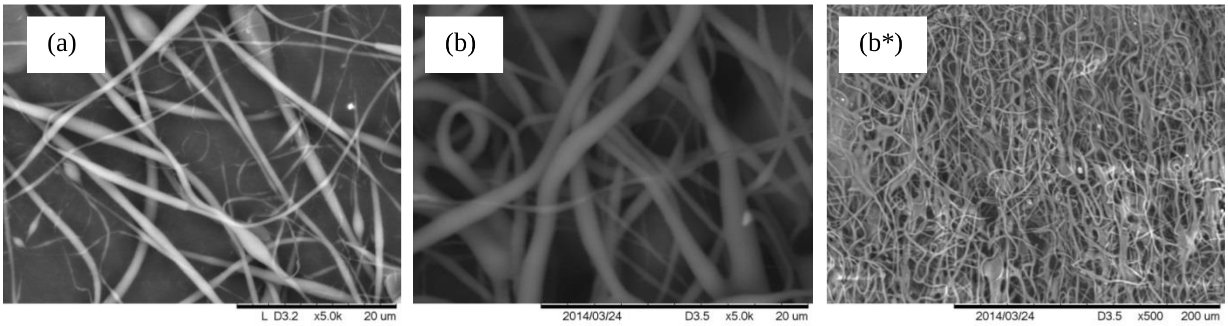


Figure 11. SEM micrographs of electrospun PVDF-530 fiber mats at 20 kV, 20 cm, pumping rate is 1 ml/h. Solution concentration is: a) 16%; b) 20%, magnification 5000×; b*) 20%, magnification 500×.

The results of this part indicate that the fiber diameter, morphology and solution properties of PVDF strongly depend on the composition of the mixed solvent used in electrospinning.

4.2. Effect of Molar mass

Molar mass (MM) has a significant effect on viscosity, fiber sizes and morphology. As mentioned in the theory of electrospinning process, molar mass of the polymer reflects the number of entanglements of polymer chains in a solution, thus solution viscosity. And as found out before viscosity has direct effect on fiber sizes. Therefore, to study the effect of molar mass, PVDF with two different MM, namely 275 and 530 kg/mol, was taken. Behavior of PVDF-530 was shown in previous sub-chapters. PVDF-275 in 1:1 DMF/Acetone with three different concentrations of 16%, 20% and 25% were also electrospun and morphology of obtained fibers are presented in Figure 12.

As can be seen from Figure 12 (a), for low molar mass PVDF-275 no fibers are observed at concentration 16% in contrast to PVDF-530 (compare Figures 11 and 8). This is attributed to the low viscosity resulting in low viscoelastic force due to low degree of chain entanglement not able to withstand the applied electric field. It means that higher critical concentration is necessary for PVDF-275 chains to overlap and create entanglements compared to PVDF-530

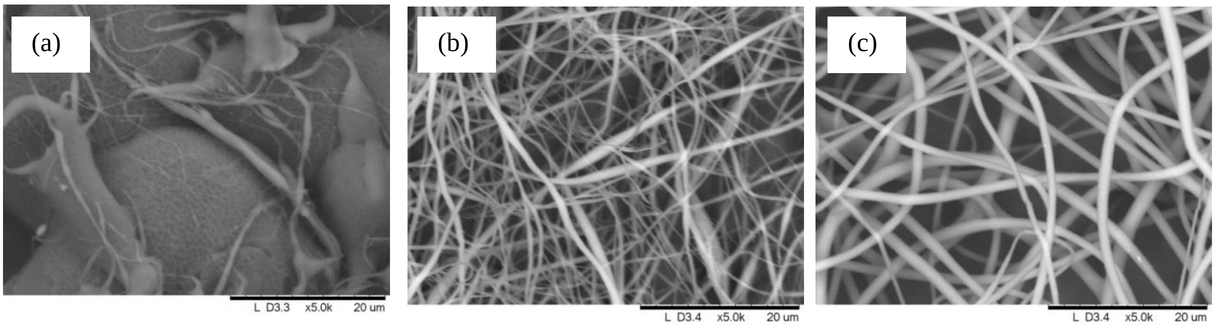


Figure 12. Morphology of PVDF-275 fibers electrospun from a) 16%; b) 20%; c) 25% solution in 1:1 DMF/Acetone obtained by scanning electron microscopy.

due to twice difference in their molar masses. Even for PVDF-530 the concentration of 16% was not sufficient to create homogeneous, not beaded and smooth fibers. At this concentration PVDF-275 only forms beads with trailing fibers. Higher concentrations as 20% and 25% of PVDF-275 initiate the electrospinning of smooth, uniform and beads free fibers. At concentrations 20% and 25% there are no meshed fibers, like it was observed for PVDF-530 on the Figure 7 or 8. Therefore, as the concentration and MM increases, occurrence of beads decreases. This is due to the increased degree of chain entanglement with the rise in MM ultimately causing an increase in viscosity and therefore higher viscoelastic force causing elongation of fibers.

The Figure 13 presents the averaged fiber diameters of electrospun PVDF-530 and PVDF-275 as function of voltages and distances. First of all, there is no, or very slight, dependences of

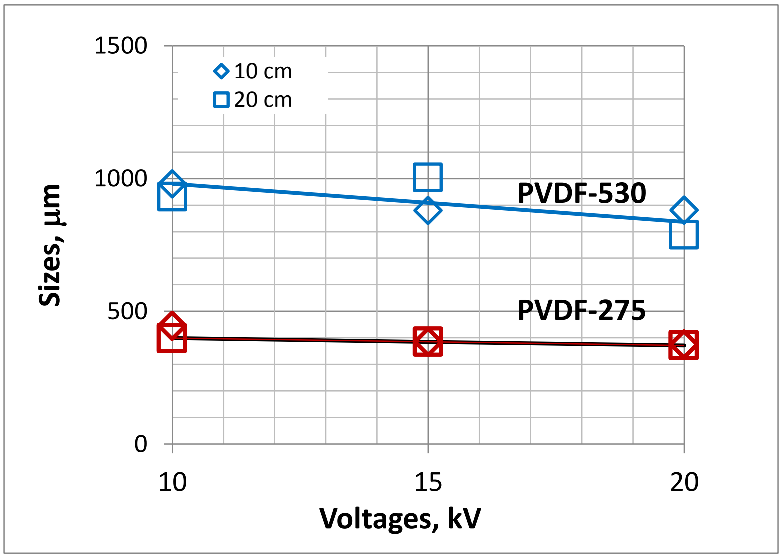


Figure 13. Effect of molar mass on fiber sizes of PVDF-530 and PVDF-275 in solutions with DMF/Acetone (1:1)

sizes on voltage and distance both for PVDF-530 and PVDF-275.

However, the mean fiber diameter shows an increase with increasing molar mass. Taken into account that measured solution conductivity and surface tension for both MM were similar, the only viscosity of solutions may be responsible for such effect. In its turn, viscosity is greatly influenced by molar mass. Figure 14 illustrates the effect of MM on viscosity of PVDF solutions. It is seen that the higher the MM, the higher is the viscosity of solution at the same polymer concentration C=20%. Viscosity increases due to increase in MM as number of chain entanglements increase. As a result, the PVDF-530 fibers are much thicker and less uniform than PVDF-275, as seen from the Figure 13 and SEM images before it.

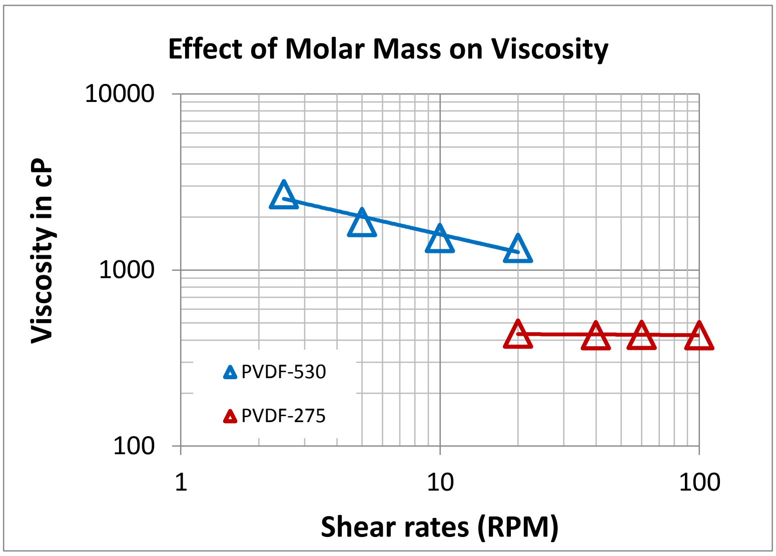


Figure 14. Shear rate dependence of viscosity for PVDR-275 and PVDF-530. Solution concentration for both polymers was 20%

4.3. Effect of added fluorosurfactant

The surfactant is usually used to reduce the surface tension of solutions. However, the effect of added surfactant on solution properties and fiber morphology of PVDF has not been anywhere studied and explained. Therefore, in this study, the influence of surfactant on the electrospinning process and morphology of electrospun PVDF nanofibers was investigated. The surfactant employed in this effort was fluorosurfactant Capstone FS-66. To all solutions of PVDF only 3wt% of FS-66 was added.

The morphologies of electrospun PVDF fibers in presence of FS-66 were evaluated using the SEM technique. SEM images for PVDF-530 in 2:3 DMF/Acetone are given in Figure 15, as example. As seen by viewing the images, all PVDF fibers are randomly distributed and exhibit fibrous web structures.

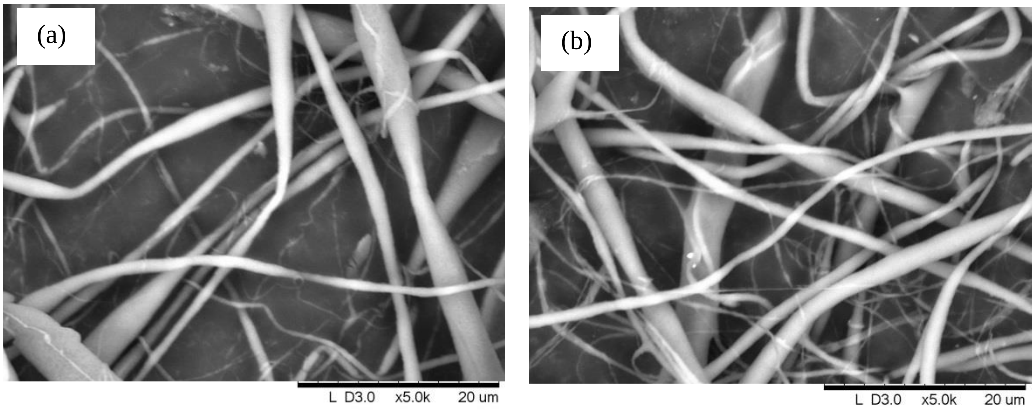


Figure 15. SEM images of fibers obtained from PVDF-530 in 2:3 DMF/Acetone, concentration 16%. Distance used 20 cm. Applied voltage is 10 kV (a) and 15 kV (b).

Comparing morphology of PVDF-530 with and without FS-66 (compare Figures 15 and 6) it is clear seen that morphology is not sufficiently affected by addition of surfactant. Fibers are still cylindrical, but non-uniform and contains beads. However, in the presence of FS-66 the amount of beads is reduced.

Figure 16 demonstrates the dependence of averaged fiber diameter as a function of applied

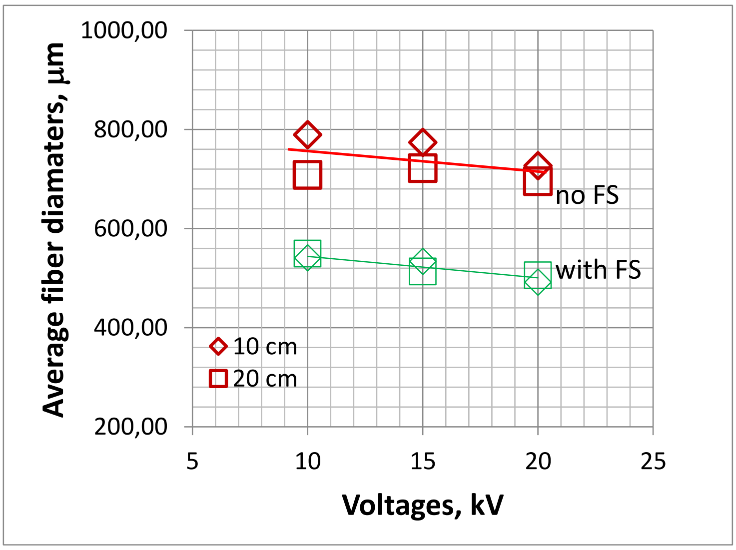


Figure 16. Effect of fluorosurfactant to average fiber sizes presented with different electrospinning conditions

voltage for PVDF-530 with and without FS. It is seen, that there is no influence of distance on fiber diameters, and only slight dependence on applied voltage can be observed. Effect of added fluorosurfactant on fiber sizes is much more pronounced: addition of FS reduces the PVDF fiber diameters in 1.5 times compared to that without FS.

In the electrospinning process, the fiber diameter is governed by complex set of chemical interactions taking place in the solution associated with viscosity, surface tension, and electrical conductivities. As shown by viewing the data given in Figure 17, the viscosity of solutions does not significantly change upon addition of the surfactant. Consequently, the changes observed in the fiber diameters can be related to both a change of solution electrical conductivity and surface tension.

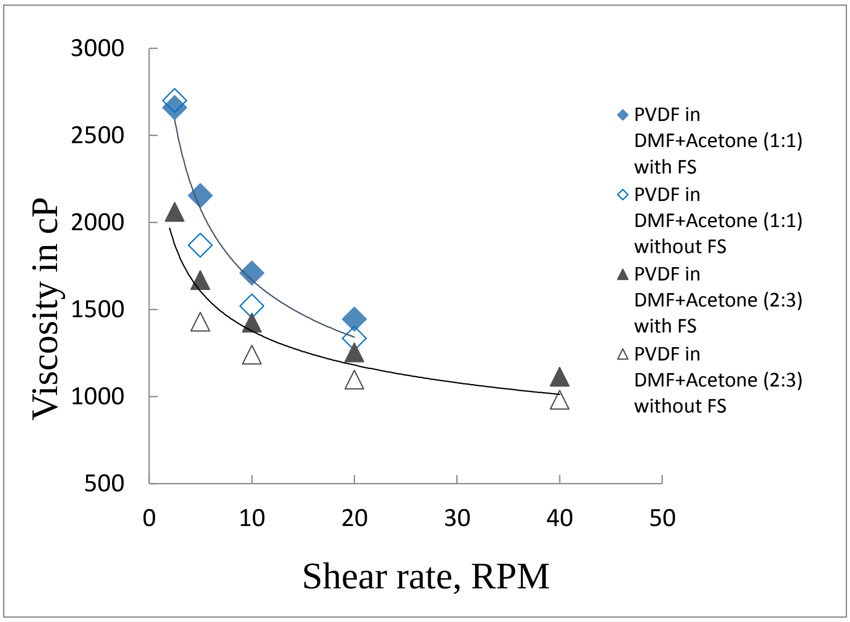


Figure 17. Shear rate dependence of viscosity for PVDF solutions with and without FS-66

Figure 18 demonstrates the effect of added FS-66 Capstone on surface tension of PVDF-530 in DMF/Acetone mixed solvent. Addition of surfactant, as expected, reduces the surface tension of PVDF solutions. Remarkably, for all the PVDF solutions surface tension was reduced in approximately two times. However, surface tension should not affect the fiber sizes, because by theory surface tension influences only the stability of jets and creation of Taylor cone in electrospinning process: the high surface tension results in big instability of jets and creation of beaded fibers.

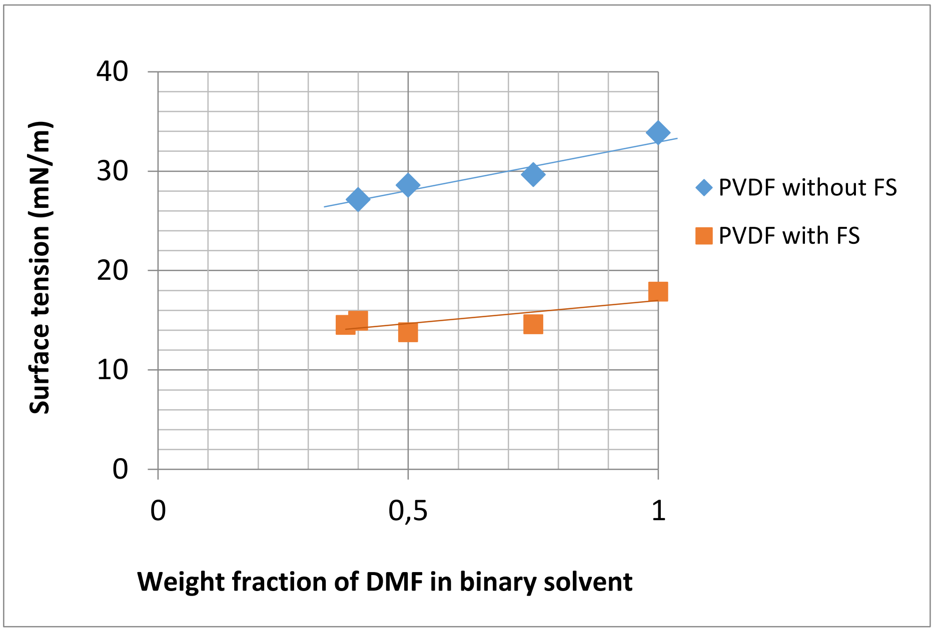


Figure 18. Effect of fluorosurfactant on surface tension

Therefore, the reduction of fiber sizes in presence of surfactant can be only associated with electrical conductivity of solutions. Table 3 shows the data of electro-conductivity of PVDF solutions with and without FS-66.

Table 3. Conductivity of different PVDF- 530 solutions

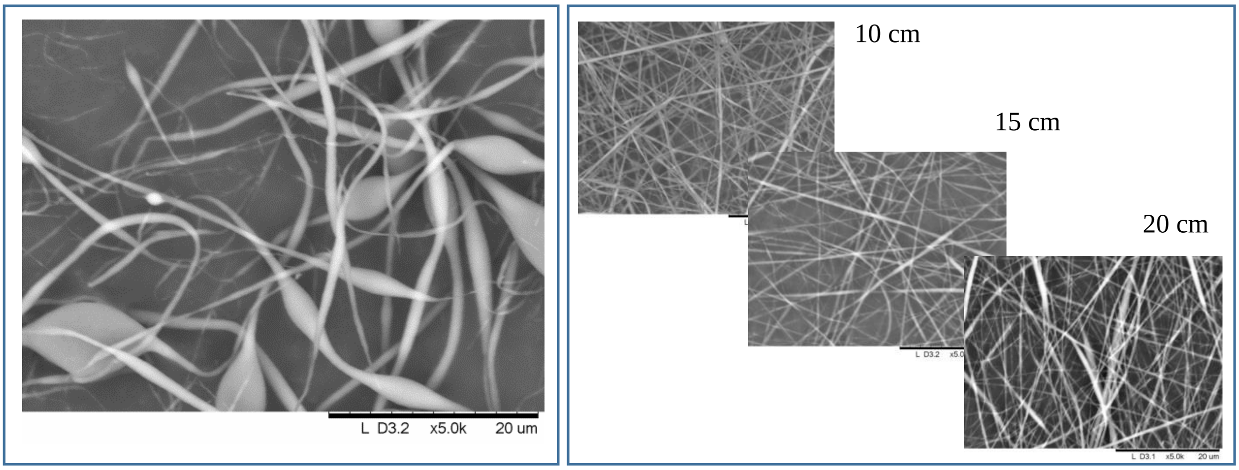
Weight fraction of DMF in binary solvent	Conductivity of solutions PVDF-530 without FS in µS/cm	Conductivity of solutions PVDF-530 with FS in µS/cm
1	1.72	26.3
0.75	2.78	27.1
0.5	5.48	37.7
0.4	3.84	34.3

From the table it is clear seen that fluorosurfactant increases the conductivity of solutions by approximately one order of magnitude (in 10 times). An increase of electrical conductivity of solutions and decrease of surface tension leads to decrease of the average fiber diameter and number of beads when the fluorosurfactant is included.

4.4 Effect of sonication on morphology and fiber sizes

Ultrasound (US) is known to be used in a wide range of chemical and physical consequences. It has the ability to assist the mass transfer between the solvent and non-solvent. Ultrasonic irradiation can contribute the mass transfer of DMF from higher concentration zone to lower concentration zone due to better molecule movement under US exposure and increase in the diffusion rate of DMF. Taken into account that used co-solvent acetone is a non-solvent for PVDF, better mass transfer of DMF in binary solvent can help to improve PVDF solubility in mixed solvent, which can create additional chain entanglements, and more stable electrospinning process can be achieved.

In this work solution of PVDF-530 in 2:3 DMF/Acetone with FS was ultrasonically stirred during 4-5 h until fully transparent homogeneous solution is prepared. The prepared solution was successfully electrospin at various distances and voltages. Figure 17(b) shows the selective SEM images of PVDF fiber mats electrospun at different distances; applied voltage was 15 kV. The SEM images of electrospun fibers prepared at different voltages were also obtained and analyzed. For comparison Figure 17(a) shows morphology of PVDF fibers without sonication. Comparing ultrasonically treated and untreated samples the great differences in fiber morphology are observed. When samples are prepared by sonication the electrospun fibers are absolutely uniform, beads free, smooth and have cylindrical shape. Identically to results mentioned in previous sections, applied voltage and distance do not influence the fiber diameters and resulting morphology, as can be seen from the Figure 18. However, ultrasonically prepared sample demonstrates much lower fiber diameters than mechanically stirred one: after sonication the fiber size is in the range 350-450 nm *versus* that before sonication it was in the range 650-800 nm.



(a) before sonication (b) after sonication

Figure 17. SEM images of PVDF-530 in DMF/Acetone (2:3) before sonication (a) and after sonication (b). Applied voltage is 15 kV. Solution concentration is 16%.

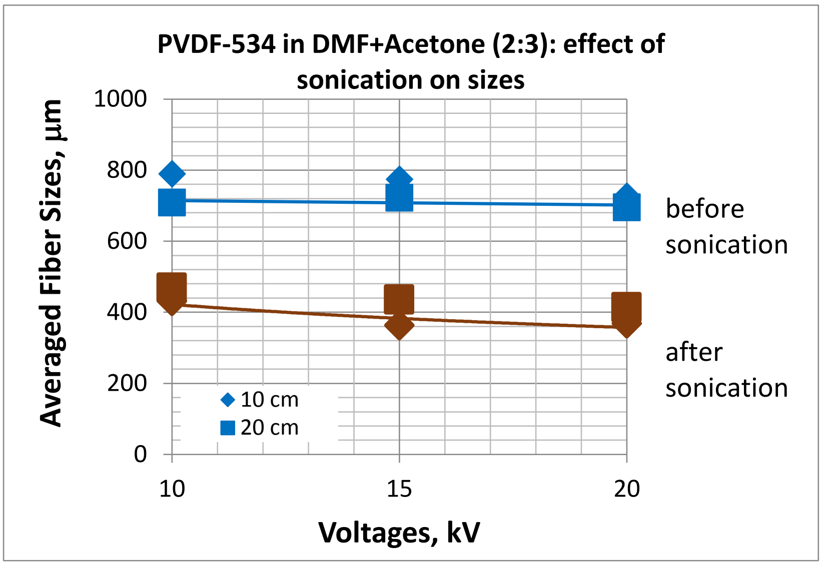


Figure 18. Fiber size dependence on voltage for ultrasonically treated and untreated 16%-solution of PVDF-530 in 2:3 DMF/Acetone.

As it has already known, the fiber diameter is governed by viscosity, surface tension, and electrical conductivities. The obtained value of surface tension of untreated samples is equal to 14.97 mN/m, for sonicated sample surface tension is 14.27 mN/m. So, it can be concluded that treated and untreated samples have the identical surface tension, because both values are within experimental error of each other. Therefore, the reduction of fiber sizes under ultrasound exposure can be associated both with electrical conductivity and viscosity of solutions. Indeed, sonication improves the conductivity from 40 $\mu S/cm$ up to 65 $\mu S/cm$. At the same, as can be observed from Figure 19, viscosity is also reduced by ultrasound treatment.

The reduction of viscosity under US exposure can be explained by the fact that in solvation, the highly polar forces in a strong localized electric field and the solvating molecules form an incompressible region around polymer chains thereby reducing the hydrodynamic volume. In its turn, reduction of hydrodynamic volume of polymer molecules is revealed in decreasing of viscosity that it is directly related to this volume. Interestingly, despite the sonicated solution has lower viscosity than untreated one the electrospun fibers have no beads, which confirms better dissolution of PVDF and creation of more entanglements under ultrasound treatment.

Therefore, application of ultrasound to polymer solution helps a lot to improve the fiber morphology, making fibers much thinner, uniform and beads-free.

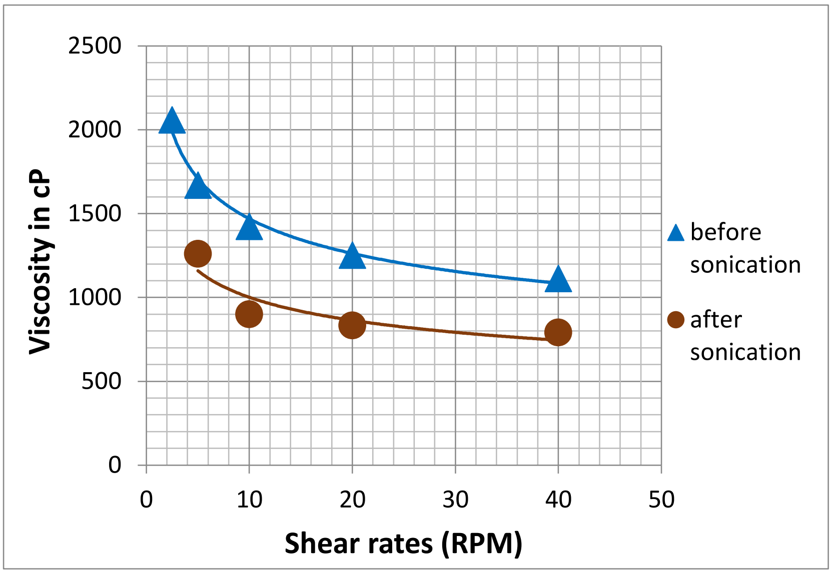


Figure 19. Viscosity of PVDF-530 in 2:3 DMF/Acetone before sonication (blue line) and after sonication (brown line). Solution concentration is 16%.

5. Conclusions

Nanofibers of PVDF have been successfully prepared by electrospinning and characterized. The effect of processing conditions such as solution viscosity, kind of solvent mixture, surface tension, MM of polymers, added surfactant, as well as applied voltage and distance to collector has been assessed by studying the characteristics in terms of morphology and fiber sizes. The following results of the work can be made:

- In pure DMF it is not possible to electrospin any fibers of PVDF at any concentrations.
- The addition of acetone decreases the surface tension of polymer solution allowing the electrospinning process to start.
- The addition of acetone decreases the viscosity of PVDF in binary solvent, causing the formation of thinner fibers
- Applied voltage (10-20 kV) and distance to collector (10-20 cm) do not affect morphology and sizes of electrospun fibers.
- PVDF with lower MM produces more homogeneous, less beaded and thinner fibers (if the concentration is kept the same).
- Addition of surfactant does not influence sufficiently the morphology of fibers, however fiber diameters are reduced.

- Sonication of solution helps to improve fiber morphology significantly and absolutely homogeneous, thin and beads free fibers are obtained.

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I am thankful for the possibility to see the kitchen side of Tallinn University of Technology.

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Picture reference

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8. Summary

The aim of this study was to find out the best conditions for producing piezoelectric PVDF fibres by electrospinning. PVDF was electrospun into fibrous membranes from its solutions in a mixture of dimethylformamide (DMF) and acetone. The morphology of electrospun membranes was viewed by scanning electron microscopy. Effects of acetone amount, polymer molar mass and viscosity, surface tension and conductivity of solutions as well as applied voltage and distance to collector were studied. The results of the work indicate that the fiber diameter, morphology and solution properties of PVDF strongly depend on the composition of the DMF and acetone used in electrospinning. Addition of acetone helps to decrease the surface tension of polymer solution and increase the evaporation rate of mixed solvent allowing the electrospinning process to start. It was established that with increasing the concentration and MM of polymer, occurrence of beads in fiber morphology decreases, due to the increased degree of chain entanglements. Addition of surfactant does not affect strongly morphology of fibers, but helps to decrease the surface tension of solution and reduce beading of fibers. It was found that sonication promotes the formation of perfect, homogeneous, thin and cylindrical PVDF nanofibers without any beading.

Kokkuvõtte

(eesti keeles)

Selle töö eesmärk on leida parimad elektroketruse tingimused PVDF kiudude jaoks. PVDF elektrokedrati kiulisse membraani lahustest, mis olid segus dimetüülformamiidiga (DMF) ja atsetooniga. Elektrokedratud membraanide morfoloogiat uuriti skaneeriva elektron mikroskoobiga (SEM). Uuriti erinevaid elektroketruse tingimuste mõjutajaid nagu atsetooni lisamine, polümeeri molaar mass ja viskoossust. Samuti uuriti pindpinevust ja elektrijuhtivust ning pinge suurust ja maandatud pinna kaugust laetud nõelast. Töö tulemused viitavad, et kõige enam mõju avaldab PVDF kiu diameetrile, morfoloogiale ja lahuse omadustele DMF-i ja atsetooni vahekord lahuses. Lisatud atsetoon aitab alandada polümeer lahuse pindpinevust, mis võimaldab elektroketrust teostada. Töö käigus kujunes arusaam, et tõstes PVDF-i kontsentratsiooni ja molaar massi, väheneb helmeste tekke kiu struktuuris. See on tingitud omakorda makromolekulide suuremast pakketihedusest. Pindaktiivse aine lisamine ei mõjutanud oluliselt kiudude struktuuri, kuid alandas pindpinevust ja helmeste teket. Selgus, et lahuse ultraheli töötlus soodustab perfektsete, homogeensete, õhukeste ja silindrikujulise PVDF nano kiudude saamist ilma helmesteta.