Nanowebs and Thin Films Based on Poly(ethylene) Oxide

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ABSTRAKT

Tato bakalářská práce je rozdělená do dvou částí, na teoretickou a praktickou. V teoretické části je stručně vysvětlen proces elektrostatického zvlákňování (princip, parametry ovlivňující proces, zařízení, aplikace vláken) a stručná charakteristika polyetylen(oxidu), polymeru, který byl v této práci použit. Prezentovány jsou také metody, kterých bylo využíváno pro další měření.

V experimentální části jsou uvedeny informace o přípravě polymerních roztoků, a také podrobné vysvětlení použitých metod (elektrostatického zvlákňování, odlévání filmů, rastrovací elektronová mikroskopie a polarizační mikroskopie). Samozřejmě získané výsledky jsou prezentovány a následně diskutovány. Hlavní poznatky jsou shrnuty v závěru.

Klíčová slova: elektrostatické zvlákňování • polyetylen oxid • nanovlákna • filmy

ABSTRACT

The presented bachelor thesis is divided into two parts – the theoretical background and the experimental work. A brief view into the process of electrospinning (principle, parameters, devices, application of fibres) and piece of information about a polymer, polyethylene(oxide), and methods, which were employed for further experiments, are presented.

In the experimental part, information about the preparation of polymer solutions and detailed description of used methodology (electrospinning, film casting, scanning electron microscopy and polarized light microscopy) is mentioned. Certainly, the presentation of the obtained results and their discussion follows, and the highlights are summarized in conclusions.

Keywords: Electrospinning • Polyethylene oxide • Nanofibres • Films

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I hereby declare that the print version of my Bachelor's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

CONTENTS

INTRODUCTION

Electrospinning is a unique technique of fabrication of non-woven webs in electrostatic field. The spun fibres can be produced in tens or hundreds of nanometers in diameter, which provide them original properties, *e.g.* large specific surface area. Despite the poor mechanical properties, the spun fibres seem to be really attractive for various applications such as filtration, tissue engineering, *etc*. Therefore, the process of electrospinning attracts the attention in both, academic as well as industrial areas.

The first knowledge, how to prepare the fibres via electrospinning, is relatively old. However, the main progress was accelerated by the invention in the last decade. The technology of electrospinning is rather simple, and the portfolio of polymers suitable for electrospinning is also quite broad. Nevertheless, the production of high quality fibres is big challenge, especially because of optimization of processing window, which is a very complex issue and still not completely understand. The lack of information together with low production rate of fibres hinders the broader industrial employment.

A goal of this study was to evaluate the relevance of polymer concentration and the intensity of electric field on the quality and size of electrospun fibres from polyethylene(oxide) (PEO) solutions. The prepared fibres were treated at various temperatures and the effect on the diameter was considered.

Besides, films were prepared by casting and dried under various temperatures, too. The impact of thermal treatment on their morphological structures was determined.

I. THEORETICAL PART

1 ELECTROSPINNING

Electrospinning is a relatively simple way how to produce fibres in diameter ranging from nano- to micrometers which are very attractive for various potential applications, such as filtration, medicine, *etc*. The history of the electrospinning started in the last century, when Anton Formhals patented his development in 1934. In the next years, series of patents describing an experimental setup for the production of fibres using an electrostatic force was presented. In 1966, Harold L. Simons patented an apparatus for production of ultra thin and very light in weight non-woven fabrics with different patterns using electrospinning. In 2003, a team around Oldrich Jirsak developed Nanospider, electrospinning device suitable for industrial scales. Thus, due to intensive research in the last years, the electrospinning is not limited to the laboratory work only, but pilot prototypes were already introduced. [1–3]

1.1 Process of electrospinning

Electrospun fibres are drawn from either polymer solutions or polymer melts due to the high electric field between a spinner and a collector. The polymer solution is placed on an electrode (anode or cathode) where is charged after the application of the high electric field. As the intensity of the voltage increases, the hemispherical surface of the polymer solution distorts into the form one or more conical shapes known as Taylor cones, depicted in figure 1. [4]

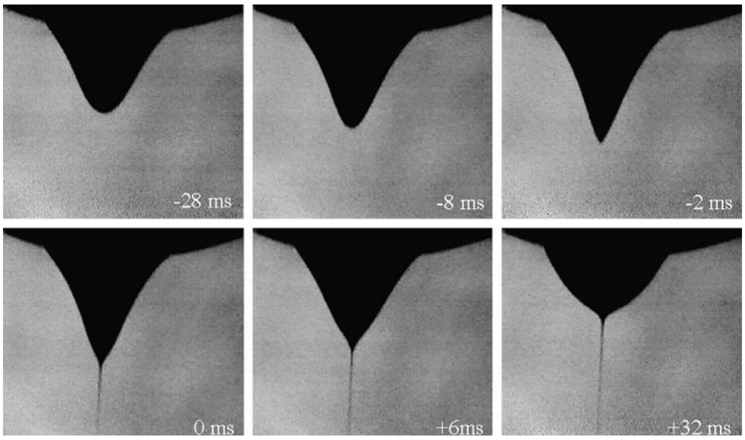


Figure 1: Taylor cone and initiation of jet in time [5].

When the intensity of the electric field reaches a critical value the repulsive electrostatic forces overcome the surface tension and the charged jet is rotationally ejected from the Taylor cone to the grounded collector (figure 1). The fibre significantly reduces its diameter as a result of high elongation rates and bending instabilities. The jet bends and follows a looping spiralling path. Simultaneously, a solvent from the solution evaporates or the melt solidifies. Thus, web of small fibres is collected on the collector of different shapes. [2,4]

1.2 Electrospun materials

A wide group of polymers can be employed for electrospinning. The proper polymer is selected in accordance to considered applications to be able guarantee required properties of the spun fibres (safety, biocompatibility, biodegradability, stability, *etc.*). [3]

Practically, a suitable candidate can be selected from the both groups of polymers, the nature and the synthetic ones. Proteins (*e.g.* collagen [10–12]), and polysaccharides (*e.g.* cellulose [6–9]), *etc.* as well as polyurethanes [13–16], polyethylene oxide (PEO) (more details in Chapter 2) [17,18], polyacrylonitrile [19,20], polyvinyl alcohol [21], polystyrene [22], polyamide [23,24], *etc.* or their blends were successfully used either for laboratory research or for industrial application.

The water-soluble polymers are preferred for application in medicine, because remaining solvents are mostly toxic and injurious to health. On the other hand, the limitation of fibres prepared from the water-soluble polymers is the need to prevent their solubility in wet environment, *e.g.* via cross-linking. [25]

1.3 Process parameters

Despite the fact that the electrospinning is rather simple technique, the production of high quality fibres is quite complicated and complex process. The process itself influences a group of parameters (system, processing and environment) whose mutual optimization can guarantee spinnability at the corresponding quality. Otherwise, electrospraying occurs and beads instead of the fibres are produced.

Type of polymer (molecular weight and its distribution, topology, *etc.*), solvent (surface tension, solubility, relative permittivity, volatility, *etc.*) or solution (viscosity, concentration, specific conductivity, *etc.*) belong to the most important system's parameters. From the processing parameters, the role of the electric field strength and tip-to-collector distance is the most crucial. Finally, the ambient parameters (temperature, humidity, *etc.*) take a role, too. [2,3]

The influence of principal parameters is further discussed in more details and summarized in table I at the end of this chapter.

1.3.1 Molecular weight and its distribution

Molecular weight dramatically influences not only the production itself, but also the geometry of spun fibres. When the molecular weight of the spun polymer is under critical value, no fibres are produced. The beads-on-string structures are spun as the molecular weight increases. To produce the high quality, circular fibres in cross section, the polymer with the optimal molecular weight has to be selected. On the other hand, too high molecular weight is reflected in higher diameter and flat-like fibre profile. [25]

The effect of molecular weight was confirmed *e.g.* in Ref. [3], where polymethylmethacrylate in various molecular weights was synthesizes and spun. As pointed out, the number of beads and droplets reducing the quality of the fibres decreased with higher molecular weights.

Also, a role of the molecular architecture (linear and branched chains) and molecular weight distribution has to be considered. The effect of the branched polymer chains on electrospinability can be controlled by their concentration [26]. And, lower concentration of highly polydispersive polymer has to be arranged for successful electrospinning [27].
Generally, the higher molecular weight increases the polymer resistance to solvent dissolution. Moreover, molecular weight of the polymer can significantly influence rheological behaviour, electrical conductivity, and dielectric properties, *etc.* [3]

1.3.2 Surface tension

Another parameter, which affects the quality of the spun fibres, is surface tension. It is given by solvent composition, because various solvents contribute differently. The impact of polymer concentration has decreasing effect, see in figure 2. [3]

Reduction of surface tension is very suitable for electrospinning because the fibres without beads or droplets are produced. Apart from the solvent composition, the surface tension can be reduced via additives, *e.g.* surfactants. And also the surface tension can be changed during the process. [28]

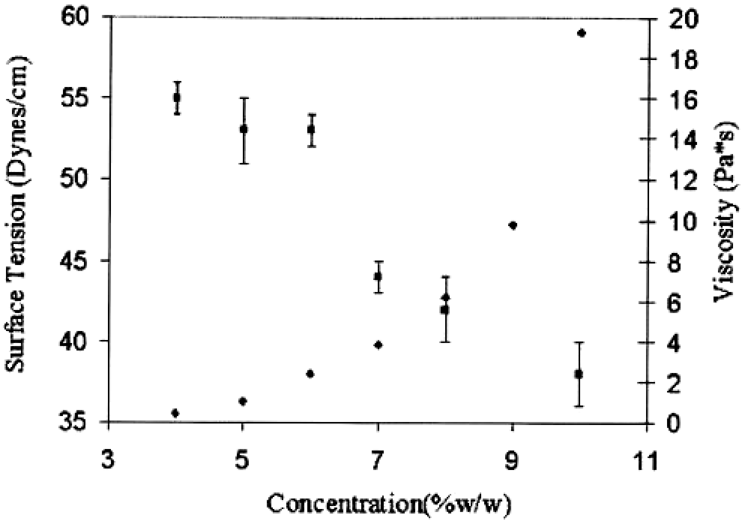


Figure 2: Dependence of surface tension (squares) and viscosity (diamonds) on the concentration for solution of PEO/water [29].

In the study [2], cellulose acetate was dissolved in either acetone or dimethylacetamide, and in their mixture. The surface tension of solution with dimethylacetamide (32.4 dyne/cm) results in beads morphology, while short cellulose acetate fibres with diameters around 1 μm were spun from the solution containing acetone (23.7 dyne/cm). And, free of beads cellulose acetate fibres were obtained, when both solvents were mixed in mutual ratio acetone : dimethylacetamide 2:1.

1.3.3 Solubility

The solubility of polymer in solvent can be predicted using solubility parameter theory. On the basis of these parameters, two groups of solvents are available – good and poor ones. The closer solubility parameters between polymer and solvent represent better miscibility because of a larger expansion of the polymer [30].

According to Hansen solubility theory, three components, namely dispersion bonds, polar bonds and hydrogen bonds between molecules play a role. For example, an influence of the employed solvent on electrospinning process for polyvinylbutyral was discussed in [30,31], where polyvinylbutyral was dissolved in good solvents (isopropanol and butanol) and poor solvents (methanol and ethanol). It was found that poor solvents contribute to high quality fibres, while the good solvents exhibit zero spinnability.

1.3.4 Concentration

The changes in polymer concentration vary solution viscosity, viscoelasticity and simultaneously the morphology of fibres. The uniform fibres can be created only using a solution with sufficient chain overlapping and entanglements. The diameter of spun fibres increases together with their uniformity at higher concentration. However, their cross section gradually changes from circular to flat-like shape. [25]

The effect of various concentration of PEO in water was studied within this work and the results are demonstrated in Chapter 5.

1.3.5 Viscosity

Also the viscosity characterizing the flow behaviour of the solution ranks among the parameters with crucial impact on the electrospinning process, because of its close correlation to concentration and molecular weight of solution. When the viscosity is too low, no continuous fibres are spun, only droplets are formed (electrospraying). But, the very high viscosity brings the difficulty during the ejection on the needle spinner, because of plugging. Thus, the optimal viscosity is required for successful process, see in figure 3. [3,28]

The effect of various viscosities with respect to fibres formation was carried out for PEO dissolved in ethanol-to-water solution and it was found a viscosity range between 0.1 Pa·s and 2 Pa·s as suitable for production of uniform fibres. Below the critical value of viscosity (under 0.1 Pa·s), droplets were spun (sprayed) only [3].

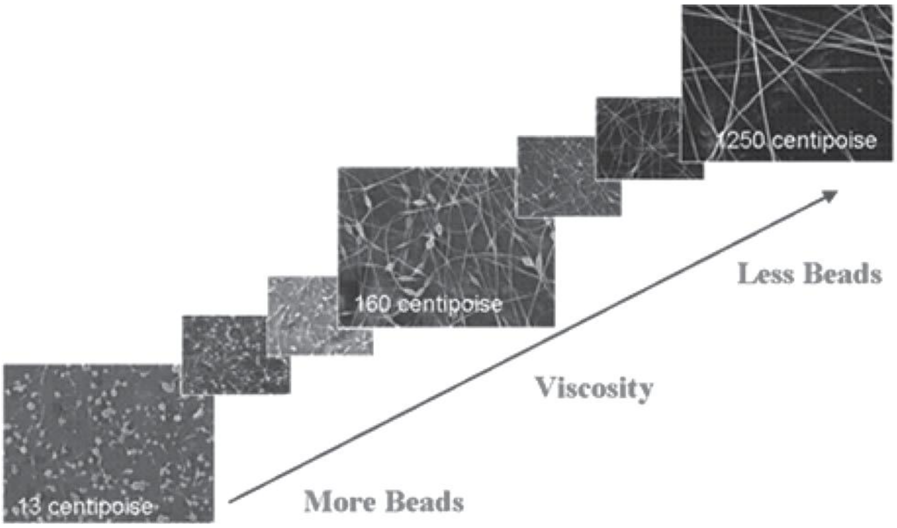


Figure 3: SEM pictures of electrospun fibres differing in solution viscosity

(1 cP = 10^{-3} Pa·s) [2].

1.3.6 Intensity of electric field

Electrospinning process is initiated by the electric field, where the spun fibres serve as charge carriers and close the electric circuit. Thus, the intensity of applied voltage between the electrode and the collector plays a fundamental role among all processing parameters (figure 4).

As shown in figure 5, charge density in solution and the shape of the initiating drop on the electrode can affect the presence of beads in fibres. [29]

The fibres prepared from PEO become rougher and contained more bead defects as the intensity of electric field increased. The charged jet of polymer solution is more accelerated at higher voltages which results in less stable jet and the number of bead defects increases. Contrary, close to the critical voltage, the flying time extends and the fibre diameter decreases. [32]

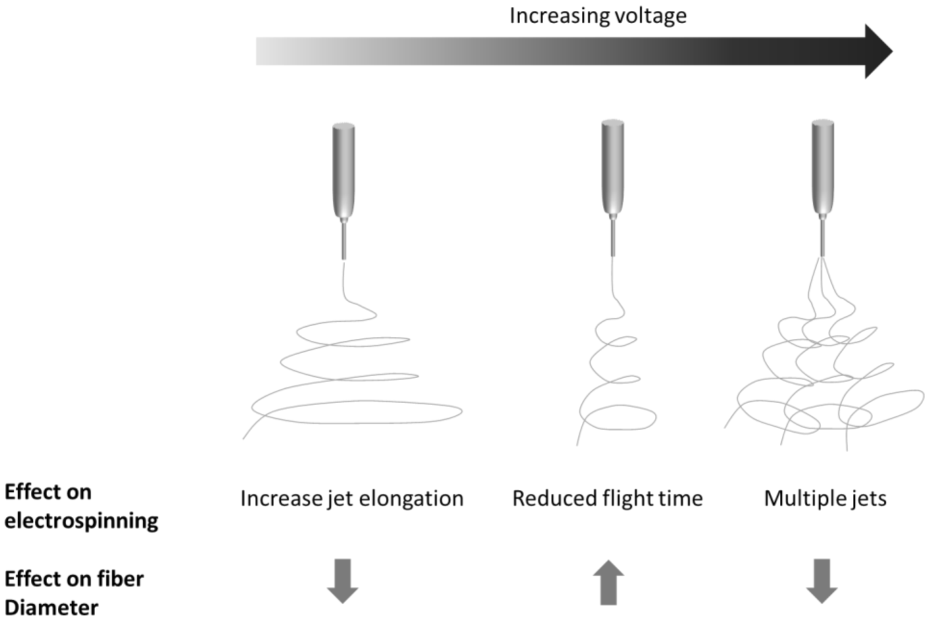
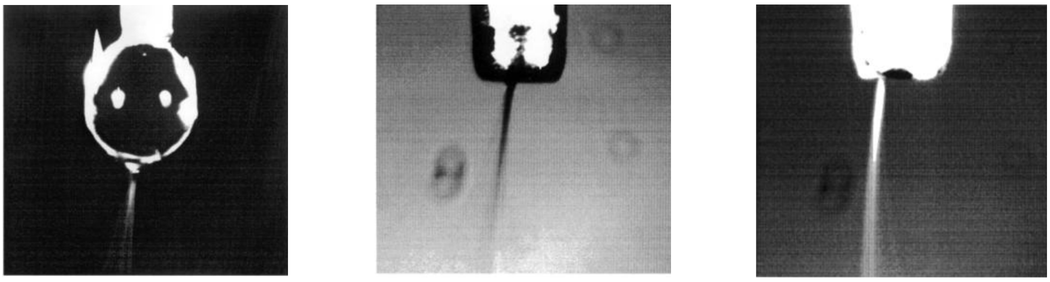
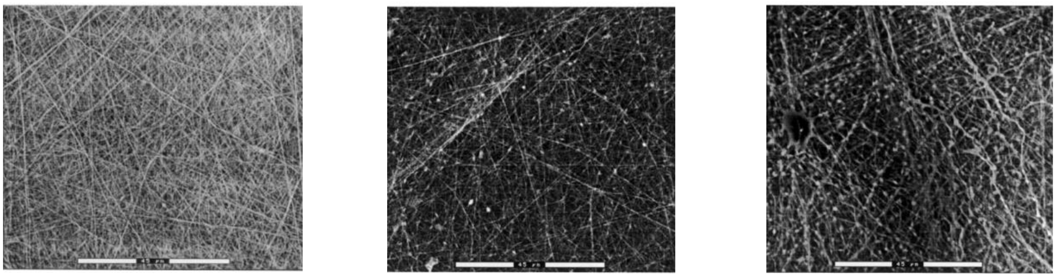


Figure 4: The effect of increasing intensity of electric field on electrospinning process and fiber diameter [32].



Initiating Jet: 5.5 kV Initiating Jet: 7.0 kV Initiating Jet: 9.0 kV



7% PEO Fibre Mat: 5.5 kV 7% PEO Fibre Mat: 7.0 kV 7% PEO Fibre Mat: 9.0 kV

Figure 5: Effect of applied voltage on fibres formation [29].

1.3.7 Distance between the tip-to-collector

The effect of tip-to-the collector distance on fibre morphology depends on the volatility. The distance between the electrode and the collector affects the jet path and thus the flying time. Generally, the fibre diameter is reduced with increasing distance. However, above a certain distance, no fibres can be created because of significant reduction of field strength. [33]

On the other hand, the minimal distance is required to provide the fibres sufficient time to evaporate the solvent or solidifies before they reach the collector. When the distance is not long enough, fresh fibres can coalesce as shown in figure 6. [33]

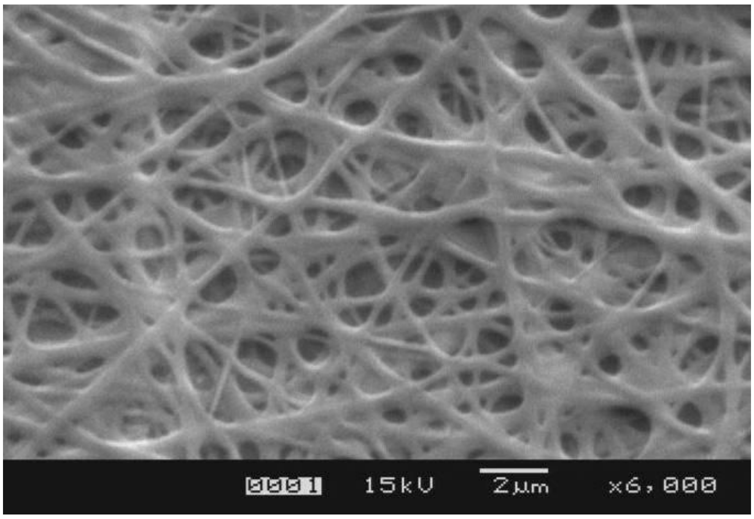


Figure 6: Fused fibres when insufficient time is given for the solvent to vaporize [33].

In practice, the effect of tip-to-collector distance on fibre morphology was observed with electrospinning of polyvinyl alcohol (PVA), gelatin, chitosan, and poly(vinylidene fluoride). As shown, flatter fibres are produced at smaller gap between the electrode and the collector. When the distance increases fibres get round shape in diameter. [3]

Table I: Processing parameters and their impact on fibre morphology [3].

Parameters	**Effect on fiber morphology**
System parameters	
Viscosity	Low-beads generation, high-increase in fiber diameter, disappearance of beads
Concentration	Increase in fiber diameter with increase of concentration
Conductivity	Decrease in fiber diameter with increase of conductivity
Molecular weight	Reduction in the number of beads and droplets with increase of molecular weight
Surface tension	No conclusive link with fiber morphology, high surface tension results in instability of jets
Processing parameters	
Tip-to-collector distance	Generation of beads with too small and too large distance, minimum distance required for uniform fibers
Applied voltage	Decrease in fiber diameter with increase in voltage
Feed rate/ Flow rate	Decrease in fiber diameter with decrease in flow rate, generation of beads with too high flow rate
Ambient parameters	
Humidity	High humidity results in circular pores on the fibers
Temperature	Increase in temperature results in decrease in fiber diameter

1.4 Types of spinner

Basically, an apparatus for electrospinning is simple. A typical spinner consists of a metal electrode, which are connected with the high voltage supply source and a collector. Nevertheless, various types of electrodes were introduced. Differences are given *e.g.* by the way of electrospinning (from the single electrode or needle) or by the quantity of spun polymer solution (roller).

1.4.1 Needle spinner

The needle spinner belongs to the simplest device which fits mainly for the laboratory testing. The syringe is filled with a polymer solution, which is pumped through a thin needle connected to the high voltage [1]. The solution is spun from tip of the needle either in vertical and horizontal alignments of needle (figure 7). [2]

There is no need to prepare large amount of the fluid what is benefit for research. On the other hand, limited volume restricts industrial applications (low productivity). Moreover, the needle clogging can easily occur when more viscous fluids are spun. [34]

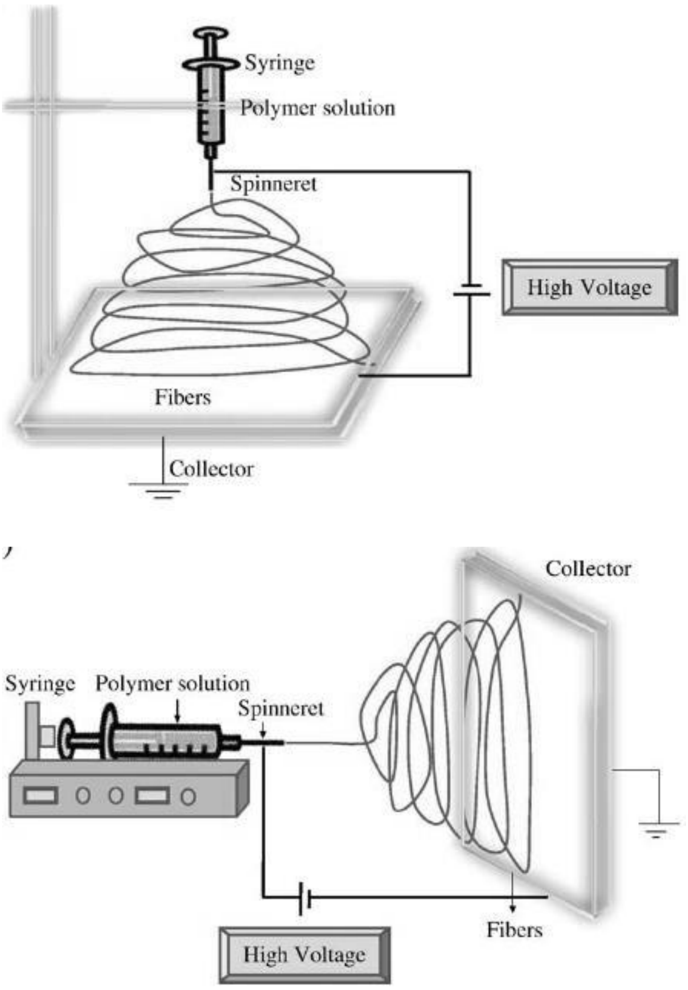


Figure 7: The needle spinner in vertical (upper) and horizontal (bottom) alignment [3].

1.4.2 Rod spinner

In contrast to the needle spinner, fibres are spun directly from the open surface of the polymer solution droplet placed on the steel rod (figure 8). Geometry of the rod, namely its diameter (usually 10 mm or less) and convexity, influence the number of Taylor cones and fibre productivity generally. The production of the fibres is discontinuous and suitable for laboratory trials only. [34]

The rod spinner was employed for the experiments presented in the experimental part (Chapter 5).

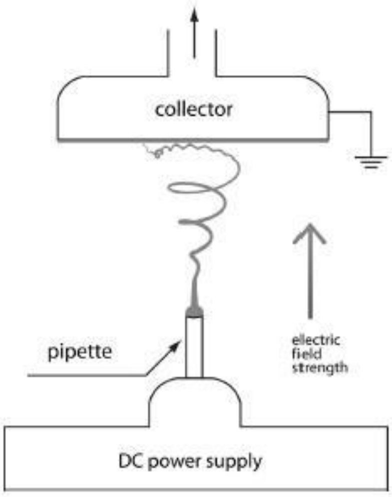


Figure 8: Scheme of rod spinner [31].

1.4.3 Roller spinner

Roller spinner is device which is employed in production of fibres on an industrial scale. In contrast to above mentioned types (with single electrode and fix collector), this spinner consists of a roller as an electrode and movable collector. [34]

In principle, the roller is dipped in a tank partially filled with a spun fluid, where rotates with defined speed. Thus, the roller is coated with a thin layer of material, which is spun from its surface and fibres are collected on the moving collector (figure 9). The jets are initiated naturally in the optimal positions along the whole roller. Together with the continuity of the process, the dimension layer of fibres can be produced. [34,35]

Naturally, different principles of the spinning apparatus have some advantages and disadvantages, which are summarized in table II.

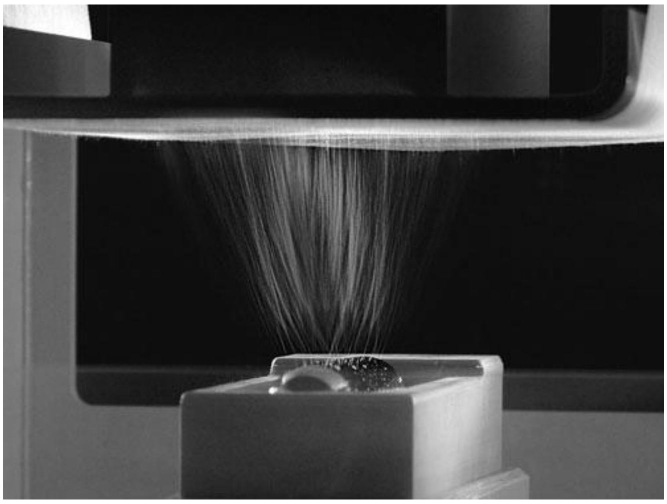


Figure 9: A roller spinner [36].

Table II: Comparison between needle electrospinning and needle-less electrospinnig [35].

Process	**Needle electrospinning**	**Needle-less electrospinning**
Advantages	Spinning solution with a wide range of viscosity	Easy maintenance
	Spinning at relatively low voltage	Easy to provide continuous nanofibrous web of various width and thickness
	Collector can be placed in any direction relative to the needle	
	Fabrication of fibers with various configurations (*e.g.* core shell, multicomponent, hollow fibre)	
	Easy to translate experimental data from spinning with a single needle	
Disadvantages	Electrical field interference between needles	Very high voltage required
	Difficult to maintain (cleaning of needle)	Difficult to maintain consistent solution viscosity owing to solvent evaporation
	Difficult to maintain a uniform feed rate through each orifice	

1.5 Nanofibres

The most characteristic feature of spun fibres is their dimension, their diameter, which varies in the range from tens to hundreds nanometres. [37] This provides them unique properties as follows:

Main properties of fibres:

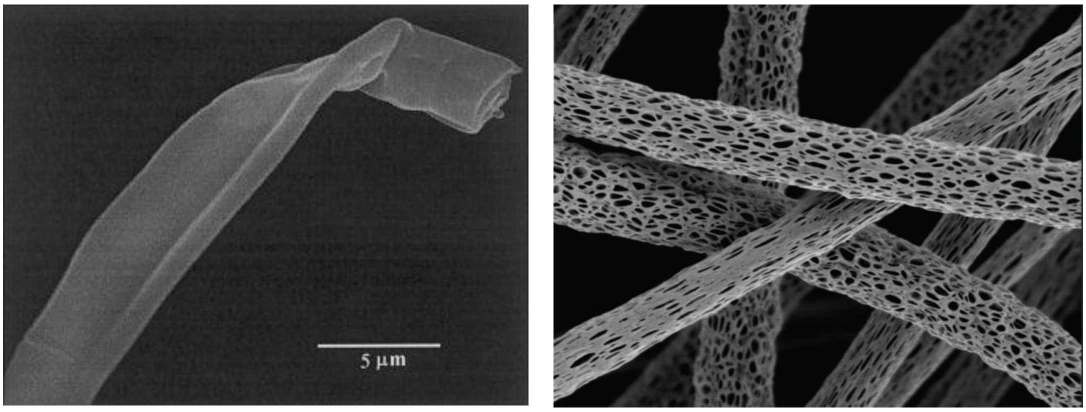
- high specific surface area
- wide range of polymers capable of spinning
- the diameter of fibres (from nanometres to micrometers)
- transparency – diameters of fibres are significantly smaller than the wavelength of light, causing the fibres invisible under an optical microscope
- excellent mechanical properties due to their weight

Certainly, fibre properties are significantly influenced by the morphology of the fibres (figure 10), which can be different depending on the processing parameters:

Morphology of fibres:

- circular
- ribbon
- porous
- smooth
- hollow
- bi-component (core-shell, side-by-side, islands/sea)

All these characteristics predetermine the spun fibres for applications in various fields, *e.g.* filtration, absorbents, fibre-reinforcement, biomedical products, or electronics and photovoltaic, *etc*.



Imagine of ribbon morphology Imagine of porous morphology

Figure 10: Different morphologies of fibres [38].

1.5.1 Filtration

To achieve a required performance of a filter, the size of the channels and pores in the fibres or membranes has to smaller than the size of the particles or droplets which should be captured in the filter.

There are two ways how to collect the pollutants in filters - either by chemical adsorption or by physical blocking, where the particles are simply blocked due to the sieve effect. [37]

In comparison to conventional filters fibres having diameter less than 0.5 µm have a much higher capability to collect the fine particles at the same pressure drop. To the typical application of electrospun filters rank air and fuel filters for automobile applications. Another example of filters is synthesized electrospun polyurethane cationomers (PUCs) containing quaternary ammonium groups with strong antimicrobial activities against Staphylococcus aureus and Escherichia coli [3].

1.5.2 Barrier textile application

Barrier textiles containing hydrophobic fibre layers, *e.g.* polyurethane or polyvinyldenfluoride, are efficiently employed as a barrier for microorganism penetration. Barrier textiles are basically prepared as a “sandwich”, where the fibre layer is enclosed between a carrier layer and a covering layer by laminating [39].

These barrier textiles are usable for surgical gowns, drapes and in disposable face mask production [39].

1.5.3 Tissue engineering scaffold

Tissue engineering is an emerging research field which involves the use of living cells. The purpose of tissue engineering is to repair, replace, maintain, or enhance the function of a particular tissue or organ. A basic principle of tissue engineering is illustrated in figure 11.

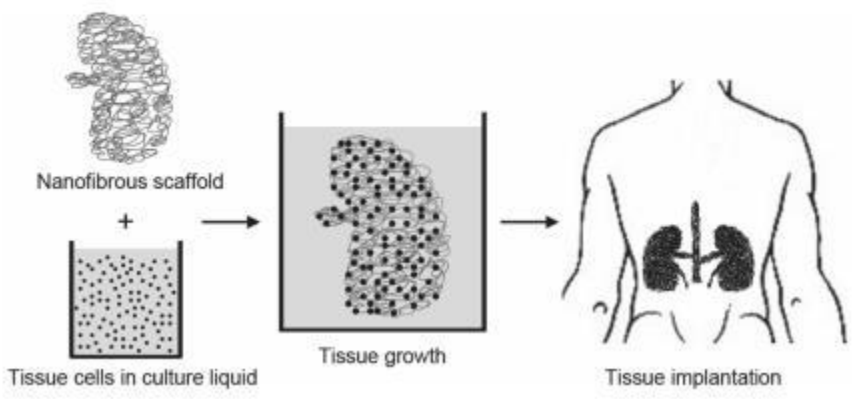


Figure 11: Illustration of tissue engineering [37]

There are a few basic requirements of scaffold, which should be fulfilled. A scaffold should possess a high degree of porosity, with an appropriate pore size distribution, have a large surface area, and be non-toxic to cells and biocompatible. Such scaffold can be produced via electrospinning, mostly from natural polymers (collagen, silk protein, hyaluronic acid, fibrinogen, *etc*.). [37,40]

1.5.4 Acoustic application

Another important property of fibres is their high acoustic absorption, especially in the low-frequency range of sound waves, where all other materials either fail or are less effective [41].

2 POLY(ETHYLENE) OXIDE

PEO is a synthetic polymer which ranks among polyethers, a class of organic compounds containing and ether group – an oxygen atom connected to two alkyl or aryl groups. PEO is readily available in a broad range of molecular weights (from hundreds to millions g/mol). As the low molecular weight is called as polyethylene glycol (PEG) and it is a viscous liquid. Above 20 000 g/mol, PEO presents waxy-like behaviour, and PEO with molecular weight between 100 000 and 5 000 000 g/mol is a white powder. [42] The density of the PEO is between to 1.15 – 1.26 g cm^{-3} [25].

2.1 Polymerization

PEO is polymerized from monomer ethylene oxide (C_2H_4O). Ethylene oxide (also oxirane) is a highly flammable, colourless gas under the room temperature. Ethylene oxide is heavier than air and it has a faintly, sweet odour.

PEO is commercially synthesized by the catalytic polymerization of ethylene oxide in the presence of metallic catalyst system [43]. The polymerization is carried out at 110 – 150 °C under elevated pressure, with KOH as a catalyst (figure 12) [44].

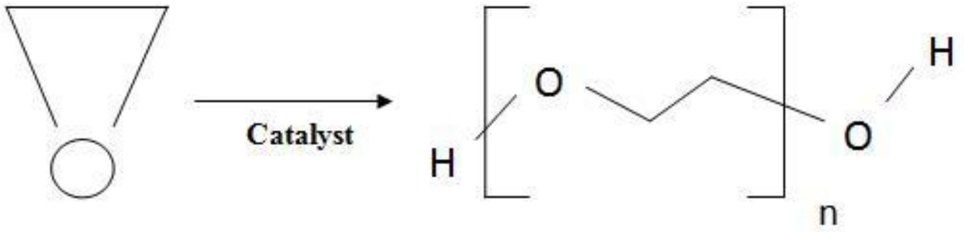


Figure 12: Synthesis of PEO [45].

2.2 Characteristic temperature

PEO is a semicrystalline polymer, so it shows not only glass temperature, but also the melting temperature.

The glass transition temperature (T_g) of PEO fractionally decreases with the increasing molecular weight in the range from -45 °C to -53 °C. [43]

The melting temperature (T_m) of PEO is above 60 °C, but it is significantly influenced by the molecular weight, especially at lower values (table III).

The auto ignition sets in the range of 280 – 330 °C and the thermal decomposition occurs above 350 °C according to molecular weight, again. [43]

Table III: The impact of molecular weight on melting temperature [46].

Molecular weight [g/mol]	**Melting temperature [˚C]**
300	-15 to -8
400	4 to 8
600	20 to 25
1 000	37 to 40
1 500	44 to 48
4 000	54 to 58
6 000	60 to 63
300 000	62 to 65
2 000 000	62 to 65

2.3 Solubility and viscosity

PEO is a water-soluble polymer. Naturally, its solubility increases with temperature. However, the solubility hinders close to the boiling point of water. Then, the phase separation may occur, and the solution becomes cloudy.

PEO can be dissolved in selected polar solvents (acetone, alcohols, toluene, *etc*.).

Generally, the viscosity of the aqueous solution of PEO depends on its molecular weight, concentration and temperature, see in table IV. PEO in a water solution give pH from 6.5 to 7.5 [43].

Table IV: The impact of molecular weight on the viscosity [43].

Molecular weight [g/mol]	**Viscosity range at 25 ˚C [Pa·s]**		
	1% solution	**2% solution**	**5% solution**
100 000	-	-	0.03 to 0.05
200 000	-	-	0.06 to 0.09
300 000	-	-	0.60 to 1.20
900 000	-	-	8.80 to 17.60
2 000 000	-	2 to 4	-
4 000 000	16.5 to 5.5	-	-
5 000 000	5.5 to 7.5	-	-
7 000 000	7.5 to 10.0	-	-

2.4 Application

The spectra of PEO application varies according to employed molecular weight – low molecular viscous liquids (PEG), waxy or the high molecular, semicrystalline solids.

PEO types with high molecular weight are processed by traditional technologies (injection moulding, extrusion, and calandaring) for water-soluble packaging films and foils. [47]

PEO is used as flocculant for water purification and lubricants. For its favourable properties, PEO is also employed in cosmetics and pharmaceutical industry as thickeners. A small addition into water solutions (0.001–0.003 %) substantially reduces the viscosity. [45,47]

PEO is also used for preparation polyurethanes, where the -OH groups have to be at the end of chain [44].

3 METHODS

In this chapter, all methods employed for the characterization of PEO fibres and films are briefly introduced.

3.1 Polarized light microscopy

Light is an electromagnetic radiation which is emitted to all directions. When it is polarized, it can be used for analysis of the crystal fragment and symmetry, phase identification, purity and homogeneity, crystal defects. This can be beneficial in polymer world for studying their morphology, too.

The polarized light microscope (figure 13) is equipped with two important parts: a polarizer and an analyzer. Polarizer is placed in the light path before the sample and allows the light waves to vibrate along their polarizing axis to pass through, while the absorbing light waves that move in other directions. Analyzer (a second polarizer) is placed between the objective lenses and eyepieces. [48]

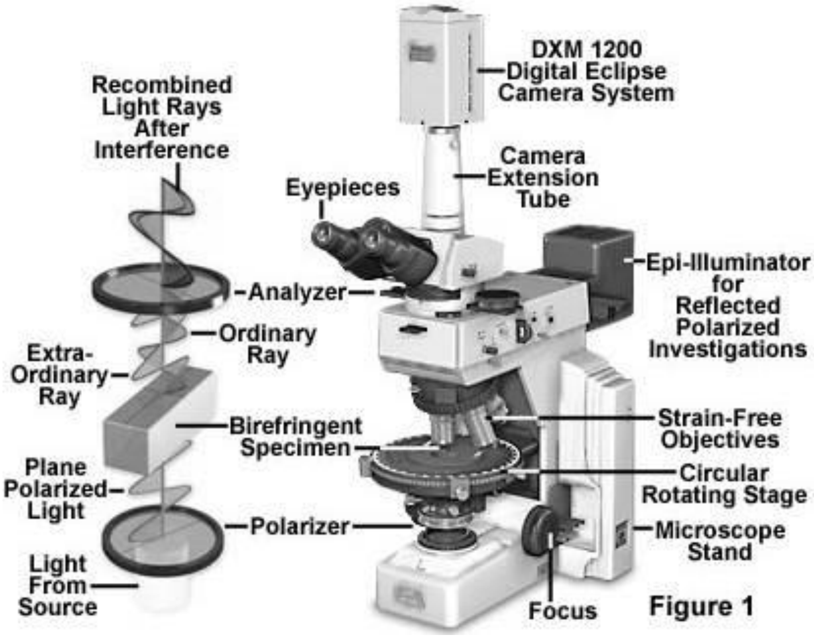


Figure 13: A configuration of polarized light microscope [48].

In principle, image contrast arises from the interaction of plane-polarized light with birefringent sample to produce two individual wave components that are each polarized in mutually perpendicular planes. After passing through the polarizer, only the light waves that oscillate in one direction are selected and others are absorbed. Then the light goes through the sample to the analyzer, where is again selected the light oscillating in one direction. [49]

3.2 Scanning Electron Microscopy

Scanning electron microscope (SEM) (figure 14) is another microscopic technique. SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of investigated material. The wavelength of electron radiation is shorter (from 0.01 to 0.001 nm) than the wavelength of visible light (from 400 to 700 nm). The higher resolution allows more details view to the polymer structure. [50]

The signals coming from electron-sample interactions carry the information about the sample including external morphology, chemical composition and crystalline structure. When the electrons interact with the sample, they produce secondary electrons, backscattered electrons and diffracted electrons (determine crystalline structures). [51]

Collected data are displayed as 2-dimensional images on a monitor connected computer. According to resolution, the area from 5 μm to 1 cm can be focused in the scanning mode. The resolution is proportional to wavelength of the used radiation. [51]

To sample preparation, the non-conducting samples have to be coated with a thin layer of conducting material (*e.g.* gold), without a conductive layer can be examined in an instrumental capable "low vacuum" operation only. [51]

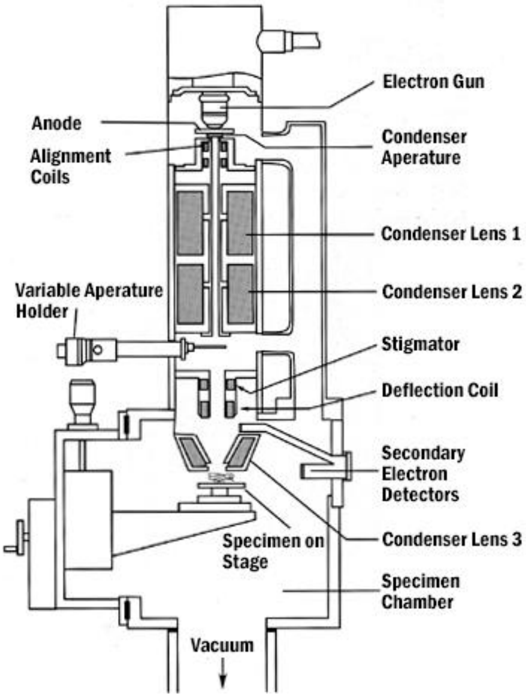


Figure 14: A scheme of SEM [52].

II. EXPERIMENTAL PART

4 MATERIALS AND METHODS

In this chapter, preparation of polymer solutions and the conditions of the measurements are discussed.

4.1 Polymer solution

Commercially available PEO (Sigma Aldrich, USA) with molecular weight Mw = 300 000 g/mol in the form of white powder was dissolved in distilled water at different concentrations (table V). PEO solutions were stirred using a magnetic stirrer (Heidolph MR Hei-Tec, Germany) with Teflon-coated magnetic cross in closed beakers. The stirring was running with mixing rate 250 rpm at 25 °C for 48 hours.

Table V: Different concentrations of PEO solution.

Concentration of the solution	**PEO [g]**	**Distilled water [g]**
7 wt.%	1.4	18.6
8 wt.%	1.6	18.4
9 wt.%	1.8	18.2
10 wt.%	2.0	18.0
11 wt.%	2.2	17.8

4.2 Electrospinning

Subsequently, all PEO solutions were electrospun using a spinner in the Institute of Hydrodynamics AS CR (figure 15) consisted of a carbon steel stick (10 mm in diameter, amount of polymer solution 0.2 ml), and a motionless flat metal collector. The tip-to-collector distance was fixed to 200 mm. The spinner was connected to a high voltage power supply (Spellman SL70PN150, USA).

The process of electrospinning was carried out at a voltage of 25, 30 and 35 kV (corresponding to the intensity of electric field 125, 150 and 175 kV/mm) at laboratory conditions at 20 ± 1 °C and relative humidity of 38 ± 3 %.

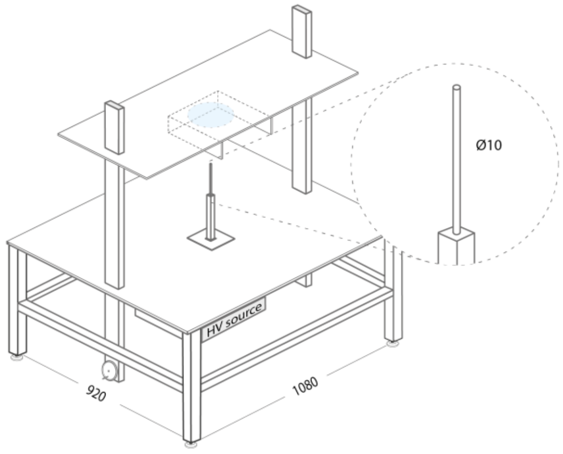


Figure 15: A scheme of home-made rod-like spinner.

Immediately after the electrospinning, the fibres were placed to an oven and treated under various temperatures, namely 20 °C (for 2 days), 40 °C, and 60 °C (for 4 hours).

4.3 Film casting

The films were prepared by casting of 2 ml of polymer solution (table V) on the Petri dish (55 mm in diameter). The solutions were treated in an oven under various temperatures, namely 20 °C (for 2 days), 40 °C, and 60 °C (for 4 hours).

4.4 Microscopic analysis

The spun fibres were analysed using the SEM microscope (Vega 3 Tescan, Czech Republic). Before analyzing, the fibres were coated with a conducting layer to increase a contrast. A mean diameter of obtained fibres was calculated from 300 measurements via Adobe Creative Suite software.

The morphology of the films was compared via optical microscope (Olympus BX41, Japan).

5 RESULTS AND DISCUSSION

5.1 The effect of PEO concentration

The effect of various concentration of polymer solution on the quality of spun fibres was studied. The fibres were spun under laboratory conditions. Before the SEM analysis, the spun fibres were treated in oven at various temperatures. In the figures 16 – 18, the SEM pictures of obtained fibres are shown.

The fibres of relative good quality were spun irrespective of solution concentration. Anyway, some beads appear on the fibres at lowest concentration (figure 16a). It seems to be a signal that the concentration approaches to the critical values, below which no fibres are produced. Contrarily, diameter of fibres increases with higher concentration of PEO in solution. This fact is confirmed in figure 21.

5.2 The effect of intensity of electric field

Without any doubt, the correct intensity of the applied electric field is a key parameter for production of the spun fibres. Here, the intensity of the electric field was changed in range 20 to 35 kV to see the impact on spun fibres from PEO solutions.

No fibres were produced at the lowest intensity of electric field (20 kV). When the intensity of the electric field gradually increased, the fibres were already spun, but they slightly reduced in diameter (figures 19, 22). Moreover, some defects appeared on their surface. The reduction in diameter is probably a consequence of more intensive elongation of fibres during the spinning; the defects could be a sign of too high surface tension.

5.3 The effect of thermal treatment

Thermal treatment of the spun fibres under various temperatures seems to be rather insignificant from dimensional point of view. The diameter of fibres changed within the statistical variance only (figure 21).

In the case of PEO films casting, the impact of temperature is naturally different and more crucial because solvent evaporation occurs and thus the various morphology is obtained (figures 23− 25).

When the temperature is low, the solvent evaporates slowly and the polymer chains, despite the limited movement, have enough time to arrange themselves to the regular structure (figure 23). As the temperature increases, the solvent evaporation continuously speeds up. Simultaneously, the polymer chains can move easier, too.

But, the arrangement to the regular morphological structure is also given by the amount of nucleus and nucleation rate, which is maximal at crystallization temperature (somewhere between glass temperature and melting temperature).

When the films were dried at 60 °C, which is quite close to the melting temperature of PEO, the nucleation process was surely less intensive than at the middle temperature (40 °C). These assumptions are in a good agreement with the results shown in figures 24 and 25, where a large amount of small spherulites is presents in the films dried at the middle temperature.

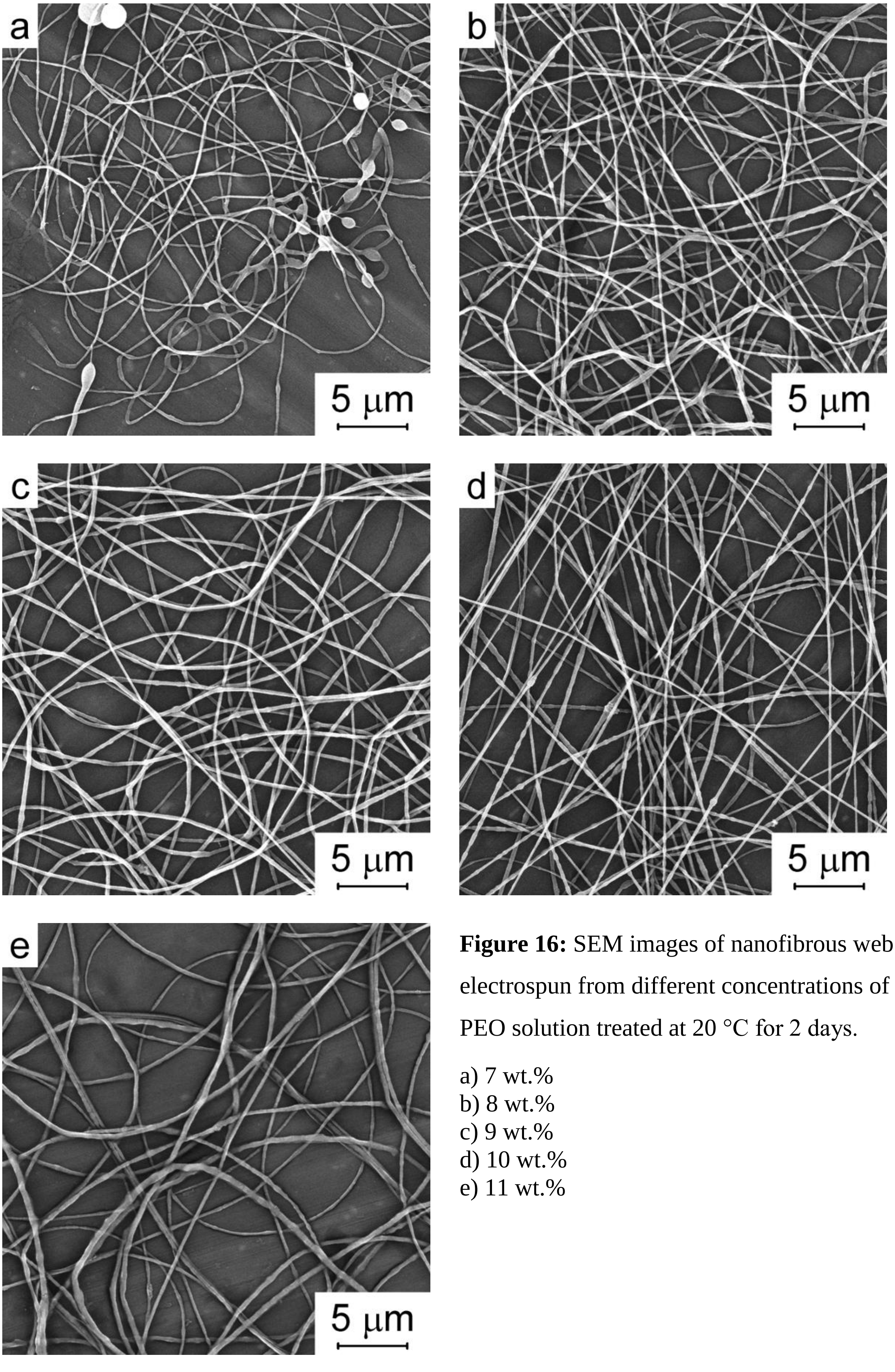


Figure 16: SEM images of nanofibrous web electrospun from different concentrations of PEO solution treated at 20 °C for 2 days.

a) 7 wt.%
b) 8 wt.%
c) 9 wt.%
d) 10 wt.%
e) 11 wt.%

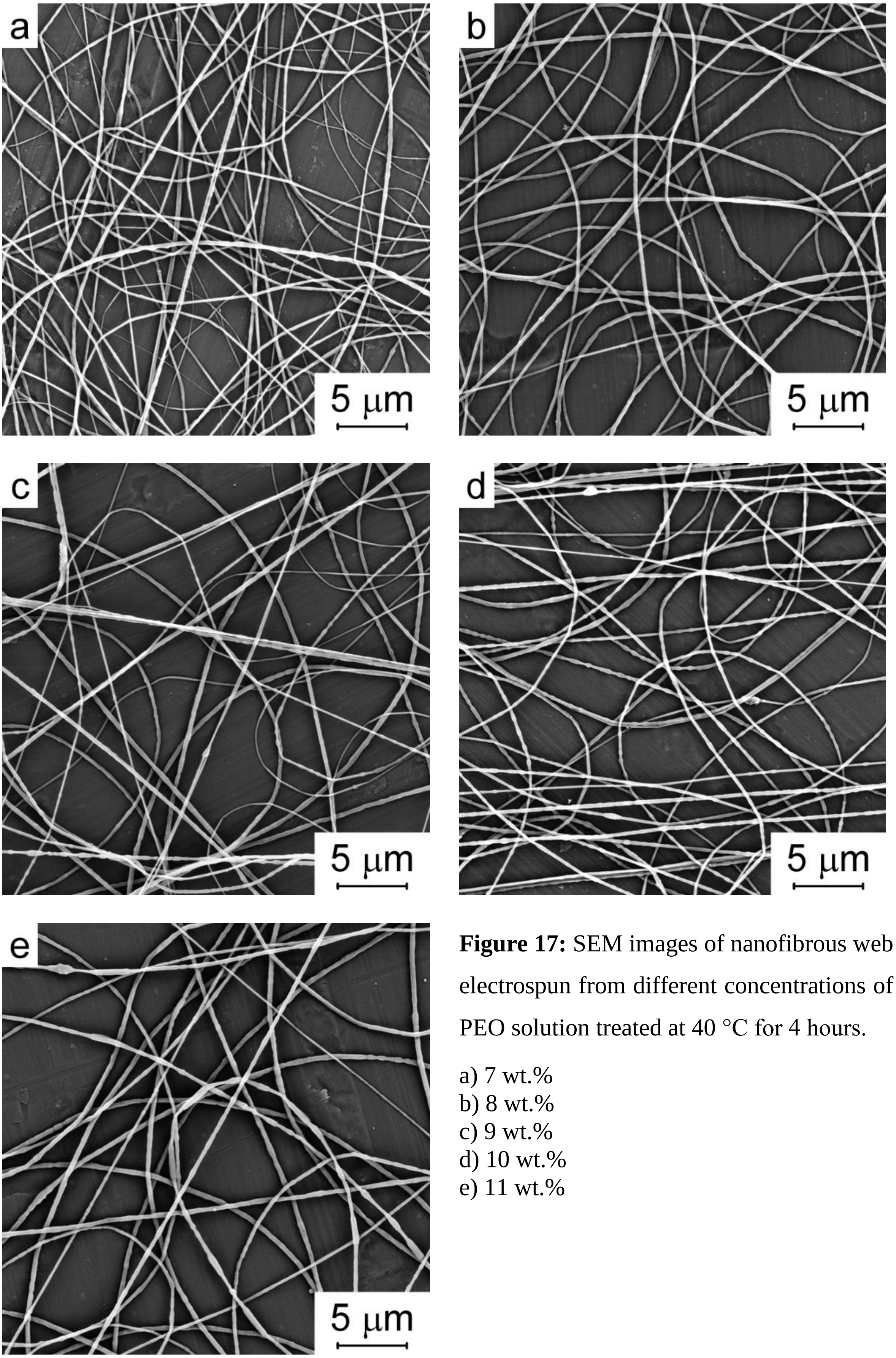


Figure 17: SEM images of nanofibrous web electrospun from different concentrations of PEO solution treated at 40 °C for 4 hours.

a) 7 wt.%
b) 8 wt.%
c) 9 wt.%
d) 10 wt.%
e) 11 wt.%

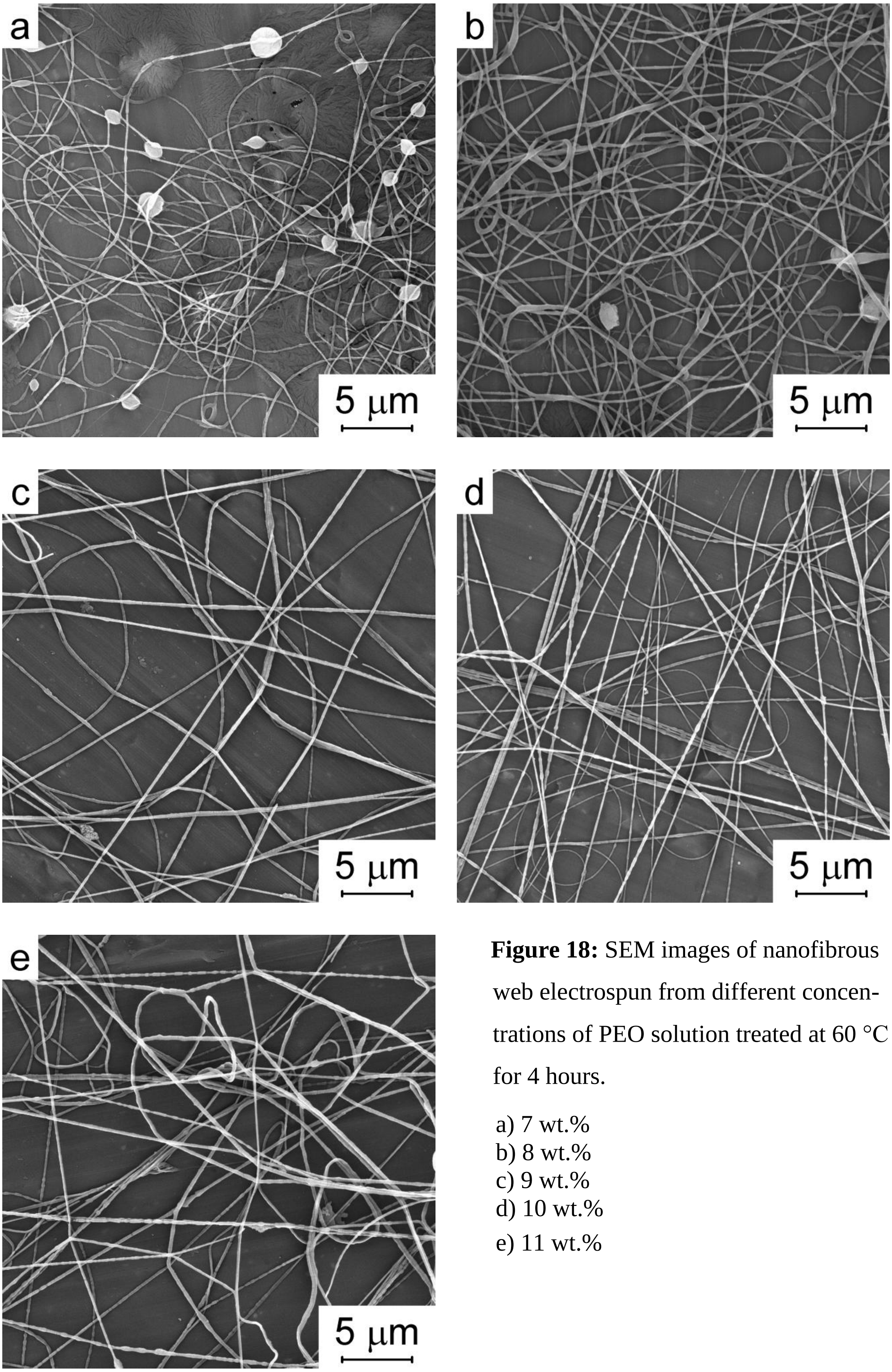


Figure 18: SEM images of nanofibrous web electrospun from different concentrations of PEO solution treated at 60 °C for 4 hours.

a) 7 wt.%
b) 8 wt.%
c) 9 wt.%
d) 10 wt.%
e) 11 wt.%

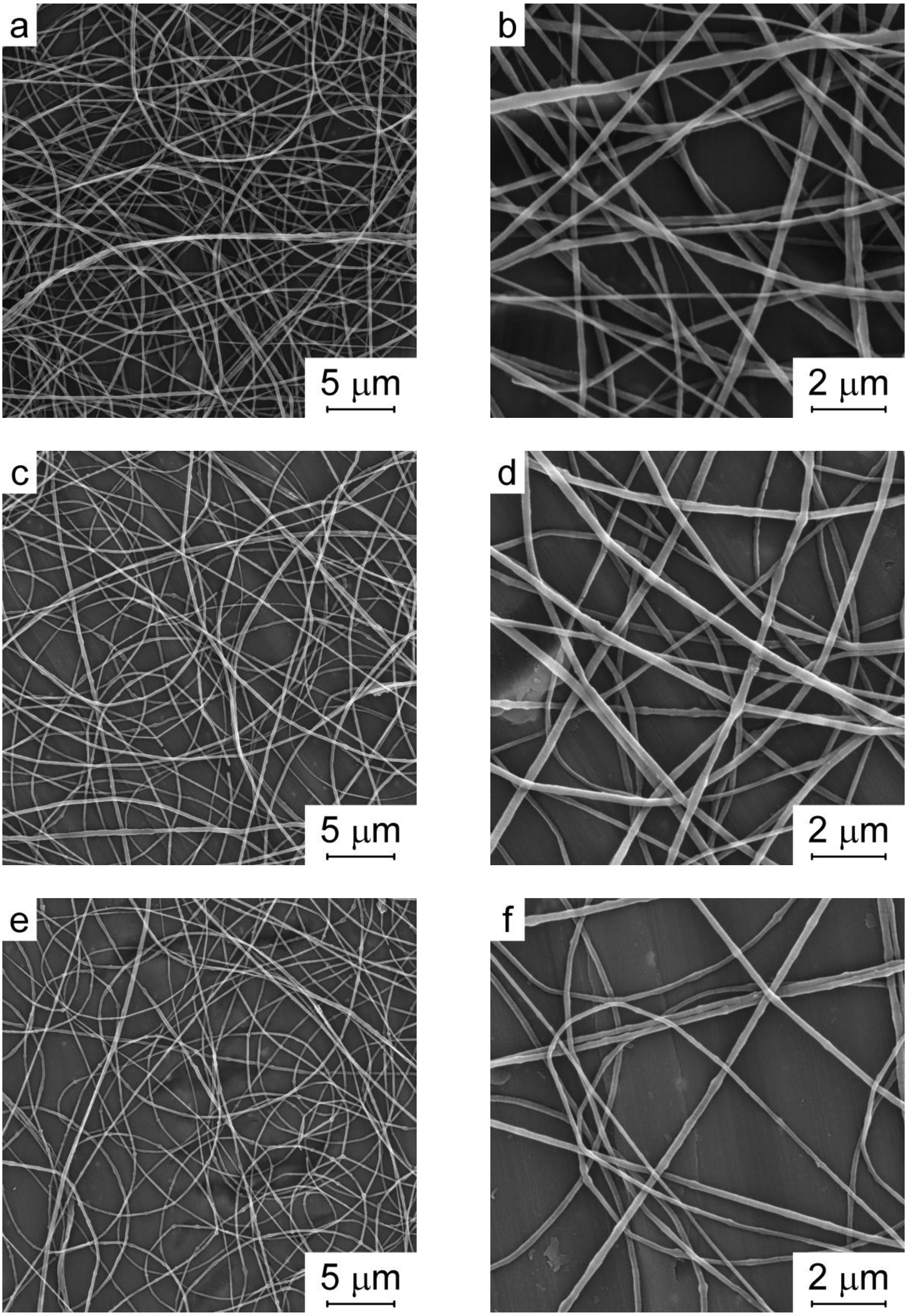


Figure 19: SEM images of nanofibrous webs electrospun from 9 wt.% PEO solution, using different applied voltage: a), b) 25 kV; c), d) 30 kV; e), f) 35 kV.

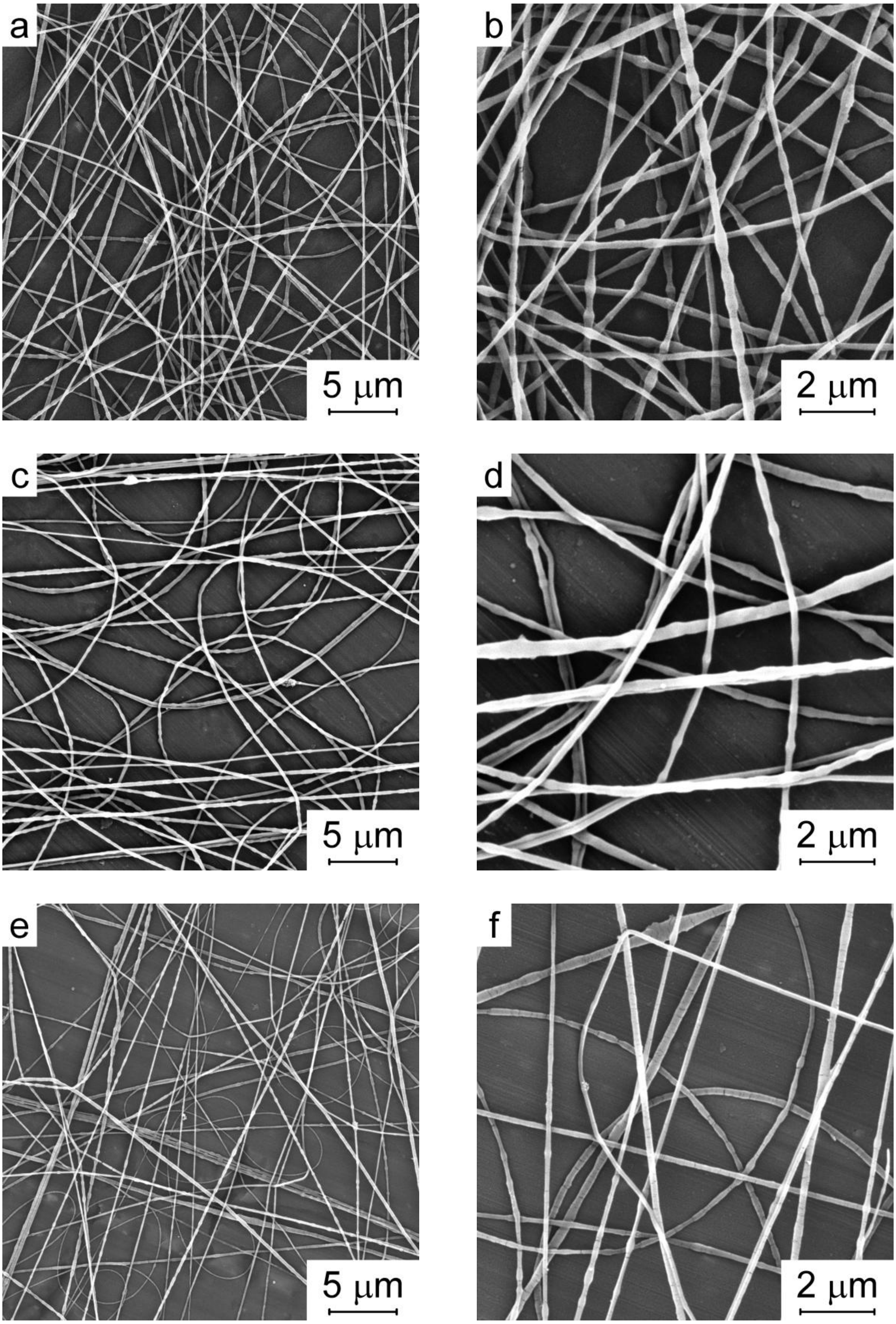


Figure 20: SEM images of nanofibrous webs electrospun from 10 wt.% PEO solution treated at: a), b) 20 °C for 2 days; c), d) 40 °C for 4 h; e), f) 60 °C for 4 h.

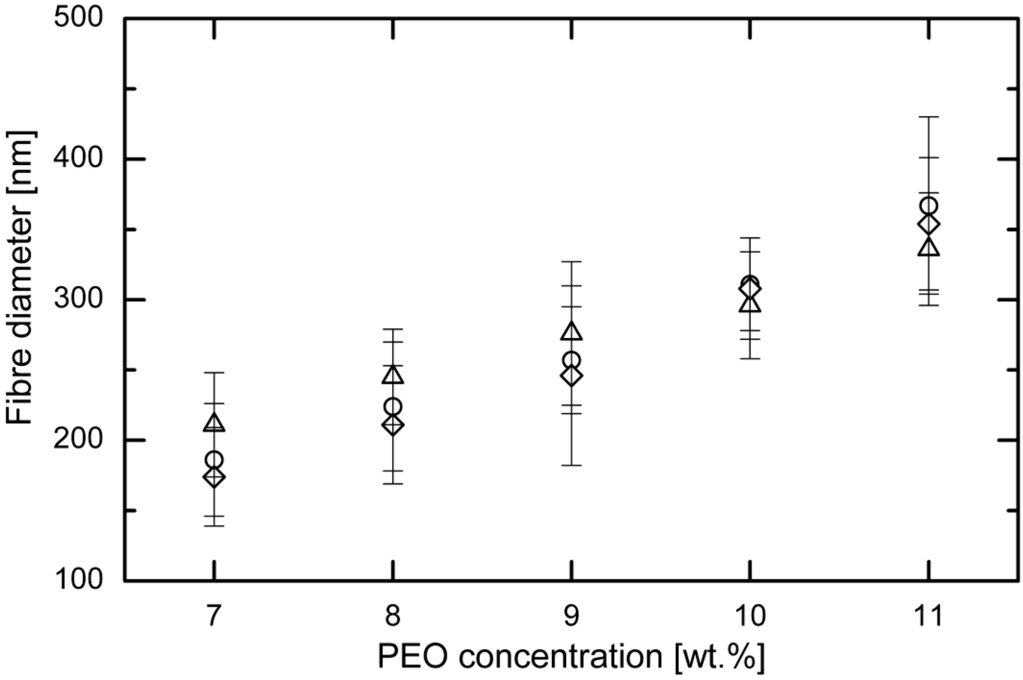


Figure 21: Fibres diameter *vs.* PEO concentration in solution employed for electrospinning. Spun fibres were treated at (○) 20 °C (for 2 days), (△) 40 °C, and (◇) 60 °C (for 4 hours).

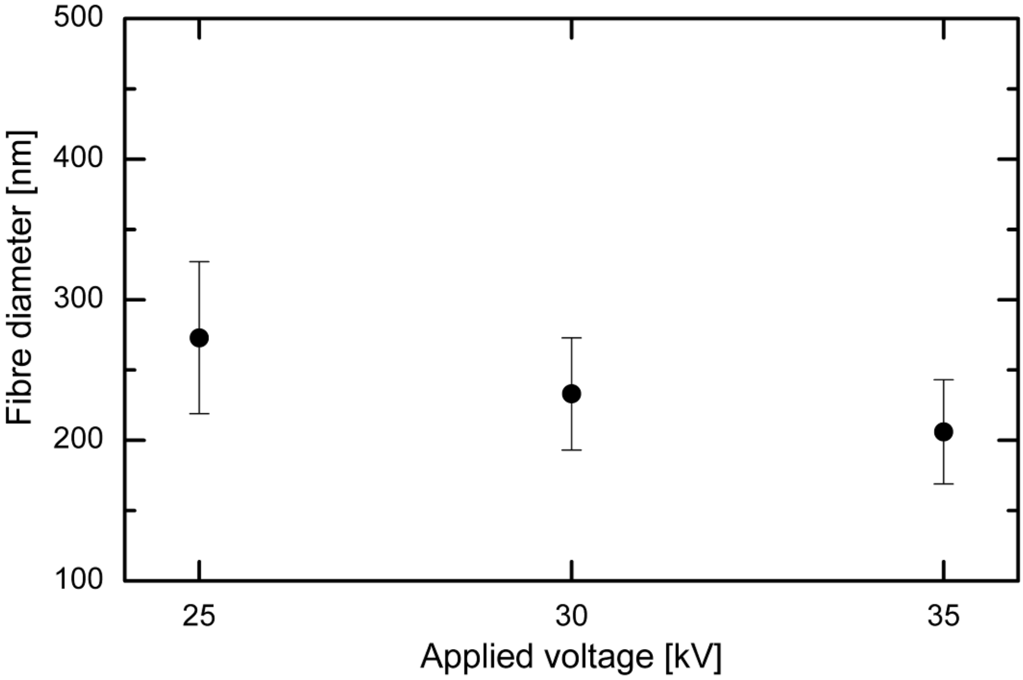
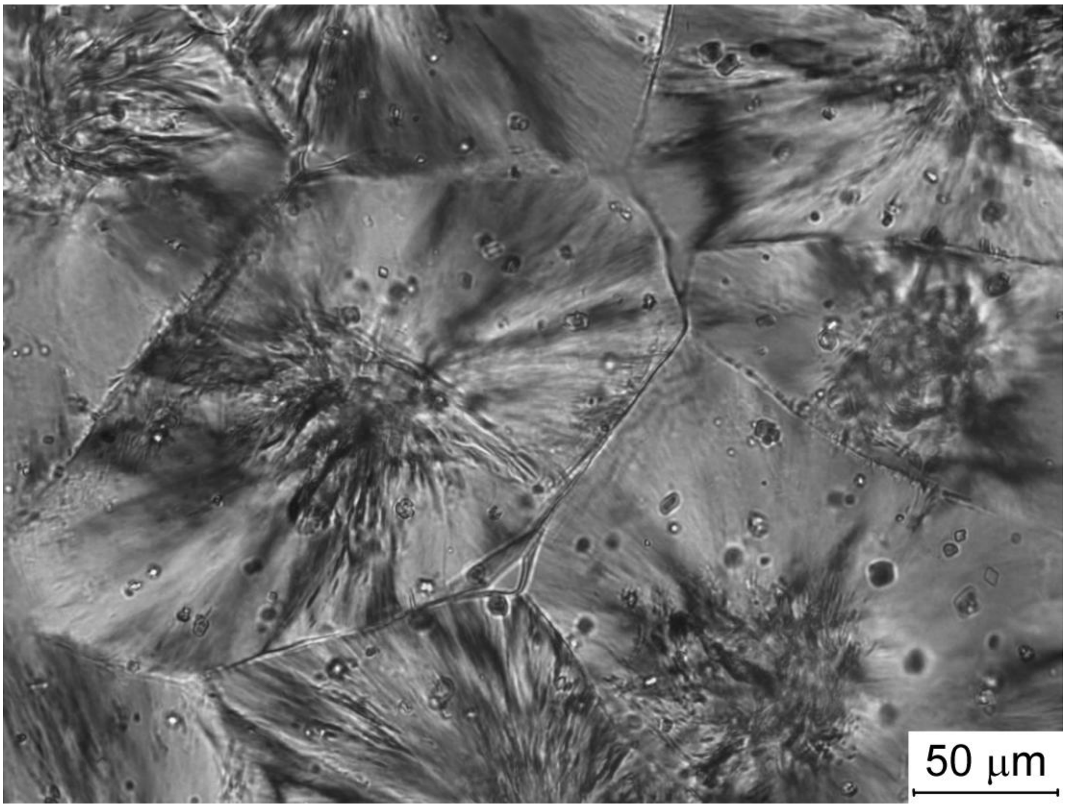


Figure 22: Fibres diameter *vs.* intensity of electric field employed for electrospinning. The concentration of PEO in solution 9 wt.%.



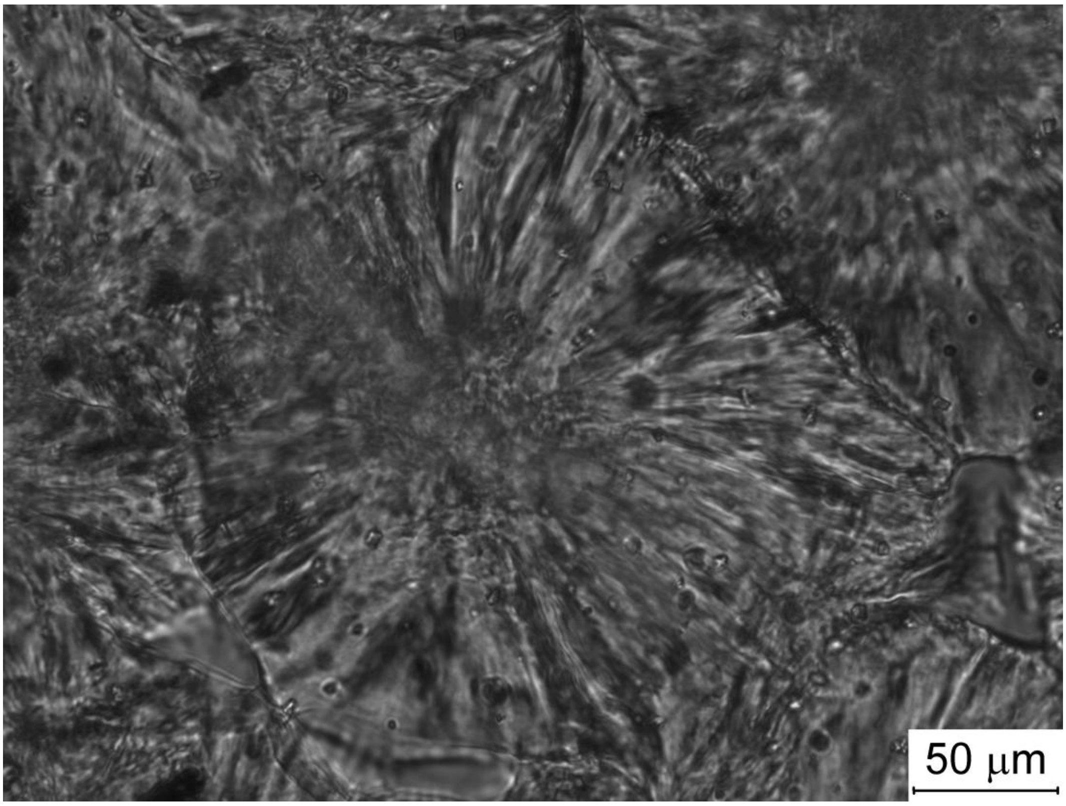


Figure 23: PEO films dried at 20 °C for 2 days: 7wt.% PEO (upper), 11wt.% PEO (lower).

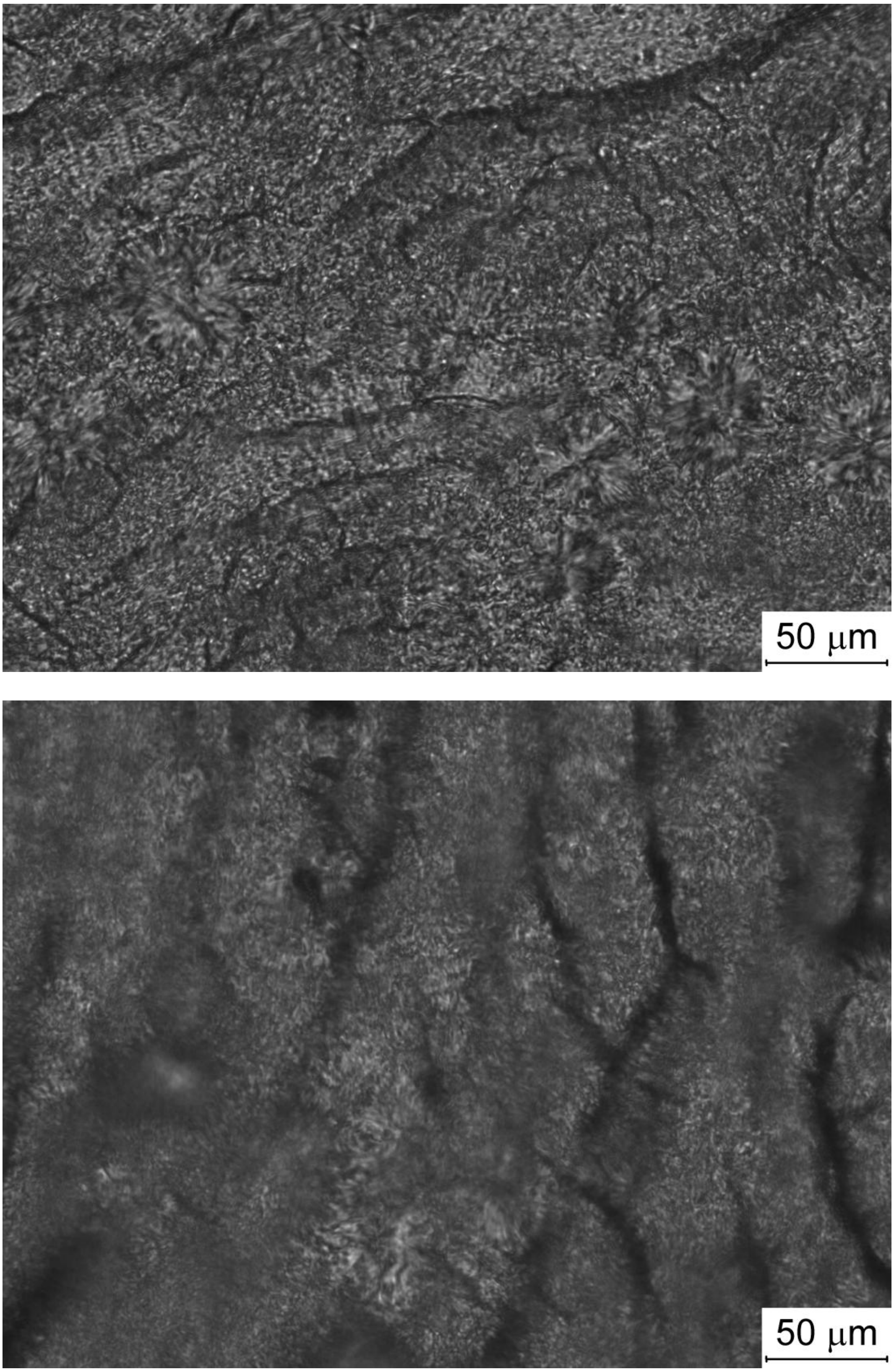


Figure 24: PEO films dried at 40 °C for 4 hours: 7wt.% PEO (upper), 11wt.% PEO (lower).

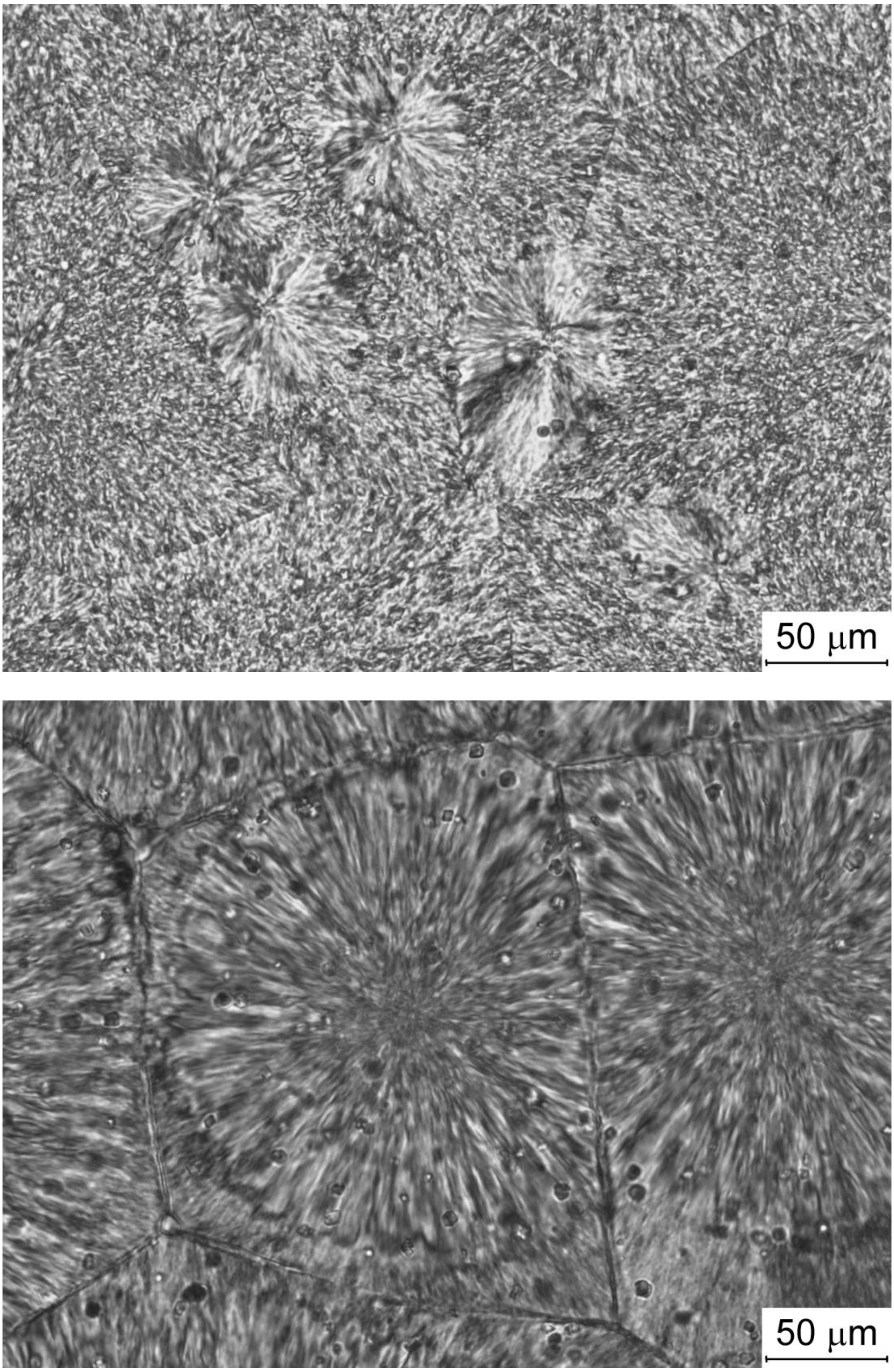


Figure 25: PEO films dried at 60 °C for 4 hours: 7wt.% PEO (upper), 11wt.% PEO (lower).

CONCLUSION

The presented bachelor thesis deals with the process of electrospinning which is a relatively easy way how to produce the fibres or membranes in the size of several tens nano- or micrometers. However, the successful production of fibres depends on optimization of parameters (material, process, and environment).

Three main parameters (effect polymer concentration, the intensity of electric field, and thermal treatment) were investigated and the results were obtained as follow:

- PEO solution in concentration from 7 wt.% to 11 wt.% are suitable for electrospinning
- Fibre diameter increases with the concentration
- Fibre diameter slightly decreases with the applied electric field
- Morphology of PEO solution used for film casting is influenced by thermal treatment

The forthcoming research in this area should be focused on the steps as follow:

- To employ another techniques (rheological, thermal) for characterization of solution used and prepared fibres/films
- Influence another processing parameters (*e.g.* tip-to collector distance) on diameter and quality of the spun fibres

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LIST OF ABBREVIATIONS

KOH	potassium hydroxide
PEG	polyethylene glycol
PEO	polyethylene oxide
PUCs	polyurethane cationomers
PVA	polyvinyl alcohol
SEM	scanning electron microscopy
T_m	melting temperature [°C]
T_g	glass transition temperature [°C]

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