**Kaunas University of Technology**

Faculty of Mechanical Engineering and Design

# The Formation and Analysis of Electrospun PVP Materials with Silver Nanoparticles

Master's Final Degree Project

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**Kaunas, 2020**

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Textile Engineering and Finishing (6211FX007)

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**Kaunas, 2020**

**Kaunas University of Technology**

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Rovena Vaičkutė

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## Declaration of Academic Integrity

I confirm that the final project of mine, Rovena Vaičkutė, on the topic "The Formation and Analysis of Electrospun PVP Materials with Silver Nanoparticles" is written completely by myself; all the provided data and research results are correct and have been obtained honestly. None of the parts of this thesis have been plagiarised from any printed, Internet-based or otherwise recorded sources. All direct and indirect quotations from external resources are indicated in the list of references. No monetary funds (unless required by Law) have been paid to anyone for any contribution to this project.

I fully and completely understand that any discovery of any manifestations/case/facts of dishonesty inevitably results in me incurring a penalty according to the procedure(s) effective at Kaunas University of Technology.

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Faculty of Mechanical Engineering and Design

# Task of the Master's Final Degree Project

Study Programme: 6211FX007 *Textile Engineering and Finishing*

**Given to the student** – Rovena Vaičkutė

1. **Title of the project –**

The Formation and Analysis of Electrospun PVP Materials with Silver Nanoparticles

*(In English)*

PVP medžiagų su sidabro nanodalelėmis formavimas elektrinio verpimo būdu ir jų analizė

*(In Lithuanian)*

2. **Aim and tasks of the project –**

The aim of the project: to form a nonwoven material from PVP nano/micro fibres containing antibacterial silver nanoparticles (Ag NPs) by means of the needleless roller electrospinning system and to investigate the influence of the small amount of Ag NPs on the structure and antibacterial properties of electrospun PVP materials.

Tasks of the project:

1. To investigate the possibility of forming nano/micro fibres from PVP solutions in water and ethanol by means of the needleless roller electrospinning equipment.
2. To evaluate the parameters of electrospun solutions with different PVP and Ag ratios.
3. To estimate the influence of PVP polymer concentration and the small amount of Ag NPs in electrospun solutions on the structure and antibacterial properties of electrospun materials.

| | | | |
|---|---|---|---|
| Project author | Rovena Vaičkutė | | 2020.04.06 |
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## Summary

Electrospinning technique is based on a self-organisation via electric charges. It is superior to other techniques due to its straightforward setup and the ability to mass-produce continuous nanofibers from various polymers and their blends. This method allows to consistently produce fibres in order to observe thinner or thicker nano/micro fibres depending on an application when changing certain parameters. With smaller pores and higher surface area than regular fibres materials, electrospun fibres materials are successfully applied in various fields as biotechnology, filtration, etc. Though, the biomedical field is one of the biggest for nano/micro fibres applications.

Polyvinylpyrrolidone (PVP) is an important biobased water-soluble polymer used in biomedical applications. It exhibits low chemical toxicity, high biocompatibility and good spinnability. Silver nanoparticles (Ag NPs) have a high antimicrobial efficiency against bacteria, viruses and other eukaryotic microorganisms and are widely used in the different kinds of textile materials. Over the past few decades electrospun nanofibers containing nanoparticles are generating notable interest in terms of the enhancement of various features. Comparing with the needle electrospinning system, the needleless one still has a high demand of further studies to be fulfilled. In regard to this interest, the aim of this study was to form nonwoven materials from PVP nano/micro fibres containing antibacterial Ag NPs by means of the needleless roller electrospinning system and to investigate the influence of the small amount of Ag NPs on the structure and antibacterial properties of electrospun PVP materials.

The findings of the project exhibited that it was not possible to produce nano/micro fibres from 4%, 6% and 8% PVP aqueous solutions by means of the needleless roller electrospinning equipment. Under the same spinning conditions nano/micro fibres were successfully formed from pure PVP ethanolic solutions and PVP with different contents of Ag NPs. It was identified that the polymer concentration in ethanolic PVP solutions had the substantial influence on the morphology and the structure of materials formed by means of the needleless roller electrospinning system. It was found that Ag NPs had the influence on the morphology of electrospun PVP materials. Thinner fibres and denser materials were formed with the higher concentration of Ag NPs. In the materials formed from 4% PVP/0,02% Ag NPs solution, 47% of the nanofibers with the diameter up to 100 nm were recorded. The antibacterial activity results exhibited the comparatively high influence of the small amount of Ag NPs against Gram-negative *E. coli* and Gram-positive *S. aureus*. The highest concentration of Ag NPs in PVP materials demonstrated the highest antibacterial effect. Although the 0,005% Ag NPs content demonstrated the inhibition zone higher than 10 mm against both types of microorganisms.

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## Santrauka

Elektrinis verpimas yra pagrįstas elektrostatinių jėgų veikimu. Šis būdas yra pranašesnė už kitus verpimo būdus dėl nesudėtingo proceso paruošimo bei galimybės masiškai pagaminti vientisas nanogijas iš įvairių polimerų bei jų mišinių. Šis metodas sudaro sąlygas pagaminti plonesnes ar storesnes gijas priklausomai nuo panaudojimo srities keičiant tam tikrus parametrus. Elektriniu verpimo būdu pagamintos neaustinės medžiagos pasižymi mažesnėmis poromis bei didesniu paviršiaus plotu negu klasikinėmis technologijomis pagamintos tekstilinės medžiagos. Šios unikalios neaustinės medžiagos yra sėkmingai taikomos įvairiose srityse, pavyzdžiui, biotechnologijoje, filtravime bei vienoje didžiausių – biomedicinos - srityje.

Polivinilpirolidonas (PVP) yra biomedicinoje naudojamas, bioskaidus, vandenyje tirpus, polimeras. Jis pasižymi mažu toksiškumu, dideliu biologiniu suderinamumu ir geru verplumu. Sidabro nanodalelės (Ag ND) pasižymi dideliu antimikrobiniu poveikiu bakterijoms, virusams ir kitiems eukariotams ir yra plačiai naudojamos įvairiose tekstilės medžiagose. Per pastaruosius kelis dešimtmečius pastebimas didelis susidomėjimas elektrinio verpimo būdu pagamintais nanopluoštais su nanodalelės dėl galimybės pagerinti medžiagų savybes jomis. Lyginant elektrinį verpimo metodą su purkštukais, metodai be purkštukų dar reikalauja nemažai tyrimų. Atsižvelgiant į šį susidomėjimą, šio tyrimo tikslas buvo elektrinio verpimo metodu su sukamuoju elektrodu velenėlyje suformuoti neaustines medžiagas iš PVP nano-mikro gijų, turinčių antibakterinių Ag ND, ir ištirti nedidelio Ag NP kiekio įtaką suformuotos medžiagos struktūrai bei antibakterinėms savybėms.

Projekte įvykdyti tyrimai parodė, kad naudojant elektrinio verpimo metodą su sukamuoju elektrodu velenėlyje buvo neįmanoma suformuoti nano-mikrogijų iš 4 %, 6 % ir 8 % PVP vandeninių tirpalų. Tomis pačiomis verpimo sąlygomis nano-mikrogijos buvo sėkmingai suformuotos iš grynų PVP tirpalų etanolyje bei etanolinių PVP tirpalų, turinčių skirtingą Ag ND kiekį. Nustatyta, kad polimero koncentracija etanoliniuose PVP tirpaluose turėjo esminės įtakos medžiagų, suformuotų elektrinio verpimo metodu su sukamuoju elektrodu velenėlyje, morfologijai ir struktūrai. Nustatyta, kad Ag ND turėjo įtakos elektrinio verpimo būdu suformuotų PVP medžiagų morfologijai. Esant didesnei šių dalelių koncentracijai susiformavo plonesnės gijos ir tankesnės medžiagos. Medžiagose, suformuotose iš 4 % PVP/0,02 % Ag ND tirpalo, užfiksuota 47 % nanogijų, kurių skersmuo yra iki 100 nm. Antibakterinio aktyvumo tyrimo rezultatai parodė palyginamai didelę itin mažo Ag ND kiekio įtaką gram-neigiamų *E. coli* ir gram-teigiamų *S. aureus* bakterijų gyvybingumui. Didžiausiu antibakteriniu poveikiu pasižymėjo medžiagos, suformuotos iš PVP tirpalų su didžiausiu Ag ND kiekiu. Tačiau net ir 0,005% Ag ND koncentracija verpimo tirpale leido medžiagoms suformuoti didesnę nei 10 mm abiejų tipų mikroorganizmų slopinimo zoną.

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## List of Symbols and Abbreviations

### Symbols

| | |
|---|---|
| a | : Area |
| Ad | : Average diameter |
| $A_p$ | : Average porosity |
| cm | : Centimetre |
| et al. | : And others |
| $g/cm^3$ | : Grams per cubic centimetre |
| g/mol | : Grams per mol |
| h | : Thickness |
| I | : Electric current |
| kV | : Kilovolt |
| L | : Working distance |
| $M_w$ | : Average molecular weight |
| m | : Mass |
| mA | : Milliampere |
| min | : Minute |
| mm | : Millimetre |
| mN/m | : Millinewton per metre |
| mPa·s | : Millipascal-second |
| nm | : Nanometre |
| No. | : Number |
| P | : Porosity |
| ppm | : Parts per million |
| rpm | : Revolutions per minute |
| T | : Temperature |
| t | : Time |
| V | : Voltage |
| v | : Speed |
| wt | : Weight |
| γ | : Surface tension |
| η | : Viscosity |
| μm | : Micrometre |
| μM | : Micromolar |
| μS/cm | : Microsiemens per centimetre |
| $\rho_b$ | : Density of bulk material |
| $\rho_m$ | : Density of electrospun material |
| σ | : Electrical conductivity |
| $^oC$ | : Celsius |

### Abbreviations:

| | |
|---|---|
| Ag NPs | : Silver nanoparticles |
| $AgNO_3$ | : Silver nitrate |
| AIBN | : Azobisisobutyronitrile |

CNC : Cellulose nanocrystal
CTCs : Circulating Tumour Cells
CTS : Chitosan
CV : Coefficient of Variation
DCE : Dichloroethane
DCM : Dichloromethane
DMF : Dimethylformamide
DSC : Differential scanning calorimetry
ECM : Extracellular matrix
E. coli : Escherichia coli
EDS/ EDX : Energy Dispersive X-Ray Spectroscopy
FTIR : Fourier-Transform Infrared Spectroscopy
INDO : Indomethacin
MRSA : Methicillin-Resistant Staphylococcus Aureus
MWCNTs : Multi-Walled Carbon Nanotubes
$NaBH_4$ : Sodium borohydride
PA : Polyamide
PAA : Polyacrylic acid
P. aeruginosa : Pseudomonas aeruginosa
PAM : Polyacrylamide
PAN : Polyacrylonitrile
PBI : Polybenzimidazole
PCL : Polycaprolactone
PE : Polyethylene
PEO : Poly(ethylene oxide)
PET : Polyethylene terephthalate
PLA : Polylactic acid
PLGA : Poly(lactic-co-glycolic acid)
PMMA : Poly(methyl methacrylate)
PP : Polypropylene
PU : Polyurethane
PVA : Polyvinyl alcohol
PVP : Polyvinylpyrrolidone
RH : Relative Humidity
S. aureus : Staphylococcus aureus
SD : Standard Deviation
SEM : Scanning Electron Microscopy
SEMEDX : Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy
TEM : Transmission Electron Microscopy
$TiO_2$ : Titanium dioxide
TBT : Titanium butoxide
UV : Ultraviolet
XRD : X-ray Diffraction
ZnO : Zinc oxide
3D : Three-Dimensional

# Introduction

Nanotechnology is an interdisciplinary field of biology, chemistry, physics and materials science. With the help of nanotechnology, nanomaterials with new properties are being developed and have been already applied in many areas in human life such as medicine, energy, electrotechnics, agriculture, cosmetics, etc. Carbon nanotubes, fluorescent nanocrystals, nano porous silica, dendrimers, graphene, and nanoparticles can be attributed to the group of nanomaterials. [1]

Electrospun nonwoven materials are unique nanostructures with an extraordinary potential in both medicinal and technical applications. Drug delivery, fibre reinforcement and filtering are just a few examples of wide range applications of nano/micro scale structures. Prior technique to produce certain materials is electrospinning which relies on self-organisation via electric charges and their interactions with an applied field. Electrospinning is superior to other techniques due to its straightforward setup, the ability to mass-produce continuous nanofibers from various polymers, and a capability to generate nanofibers with controllable diameters and compositions. However, it has been considered that due to physic behind it is not easy to understand since the properties of electrospun nanofibers can be influenced by many parameters. [2, 3]

Over the past few decades, electrospun nanofibers containing nanoparticles are generating notable interest in terms of the enhancement of various features. For instance, in certain application the conductivity could be improved by insertion of silver or lithium nanoparticles, or addition of carbon nanotubes to a certain structure may be used for the delivery of drugs at a cellular level. Especially in the field of medicine a lot of attention is given to biodegradable polymers (PVA, PLA, PVP, starch-based polymers, etc.), also usage of green solvents and the addition of nanoparticles in order to have enhanced properties. In regard to this interest, we attempted to form polyvinylpyrrolidone (PVP) nano/micro fibres with different ratios of silver nanoparticles (Ag NPs) and test the antibacterial activity of certain Ag NPs ratios. To the best of our knowledge, most of the studies of formation PVP electrospun fibres with Ag NPs had been performed using a needle electrospinning technique and only a few works had been accomplished using a roller needleless electrospinning equipment.

The aim of this project was to form a nonwoven material from PVP nano/micro fibres containing antibacterial Ag NPs by means of a needleless roller electrospinning system and to investigate the influence of the small amount of Ag NPs concentration on the structure and antibacterial properties of electrospun PVP materials.

Tasks of the project:

1) To investigate the possibility of forming nano/micro fibres from PVP solutions in water and ethanol by means of the needleless roller electrospinning equipment.
2) To evaluate the parameters of electrospun solutions with different PVP and Ag rations.
3) To estimate the influence of PVP polymer concentration and small amount of Ag NPs in electrospun solutions on the structure and the antibacterial properties of electrospun materials.

## 1. Literature Survey

The part focuses on electrospinning process in more detail, presents the research works performed until now and demonstrates the overview of the field which is under analysis.

### 1.1. Electrospinning Process

In 1902 an electrospinning process was described for the first time by J. F. Cooley in United States. The patent was called "Apparatus for electrically dispersing fibres". The scientist described the method of using high voltage power supplies to form yarn. Since this early time it was admitted that to generate a fibre rather than a droplet, fluid must be sufficiently viscous, the solvent has to be volatile enough to evaporate and allow the regeneration of a solid polymer, and the electric field strength has to be within a certain range. [4]

The term 'electrospinning' was first generated in 1995 by Doshi and Reneker. From 2002 a strong growth is presented in this area by plotting the number of scientific papers on the subject published every year. Various outstanding characteristics of electrospun nano/micro fibres are characterised including high surface area per unit mass (about 1–100 $m^2/g$), light weight, tuneable pore size, high permeability, relatively good mechanical strength, high porosity, high aspect ratio up to 1000, flexibility in surface functionalities. [4, 5]

Electrospinning is a simplistic, cost-effective, and an adaptable method that uses the electrically charged jet of polymer solution to produce fibres with diameters ranging from micro- to nanometres. Electrospun nano/micro fibres are created from the electrically charged jets of polymer solutions or polymer melts. There are two standard electrospinning setups, horizontal and vertical. A typical electrospinning setup involves a high voltage supply, a needle or spinneret (e.g., a pipette tip), a syringe pump, and a grounded oppositely charged surface for fibres to be collected on (a metal screen, plate, or rotating mandrel) (see Fig. 1). The process is conducted at room temperature with atmosphere conditions. Self-assembly is electrospinning is controlled by Coulomb interactions between charged elements of the fluid. Electrospinning can produce a wide range of morphologies including hollow tubes, highly aligned fibres, and even 3D shapes. [2, 6, 7]

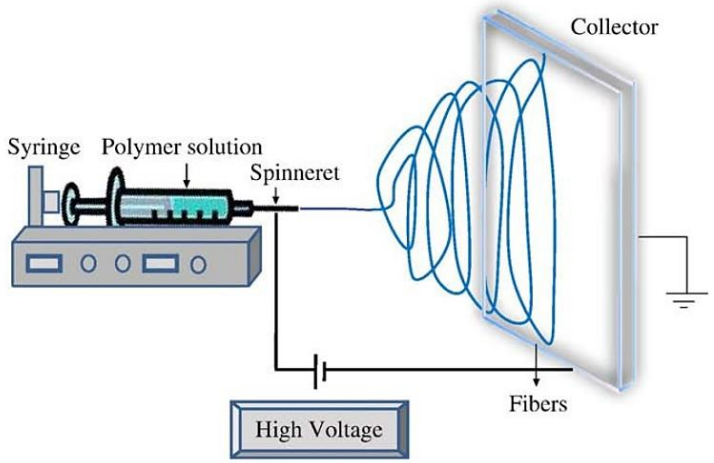


Figure 1. The schematic view of electrospinning apparatus. Horizontal set up [8]

In the electrospinning process, a polymer solution maintained by its surface tension at the end of a capillary tube is subjected to an electric field and an electric charge is induced on the liquid surface due to this electric field. When the critical value of applied electrical field is reached, the repulsive

electrical forces conquer the surface tension forces. Ultimately, the charged jet of a solution is ejected from the tip of the Taylor cone and the unstable and rapid whipping of a jet occurs in a space between the capillary tip and the collector, thus it leads to the evaporation of a solvent leaving a polymer behind. [7]

### 1.1.1. Parameters Affecting Electrospinning

The installation and all selected parameters are the most significant for the process of electrospinning. All the parameters affecting electrospinning process are divided into the three main categories (see Table 1):

1. properties of the solution used as the feedstock (solution parameters),
2. parameters associated with the design, geometry and operation of the electrospinning apparatus (processing parameters),
3. atmospheric and other local processing conditions (environmental parameters). [4]

Table 1. The parameters of electrospinning process [4]

| **Solution parameters** | **Process parameters** | **Environmental conditions** |
|---|---|---|
| Viscosity | Electrostatic potential | Temperature |
| Polymer concentration | Electric field strength | Humidity |
| Molecular weight of polymer | Electrostatic field shape | Local atmosphere flow |
| Surface tension | Working distance (between needle and collector) | Atmospheric composition |
| Electrical conductivity | Volume feed rate | Pressure |

The most affecting parameters are solution ones as viscosity, surface tension, electric conductivity and the dielectric constant of a solvent. It influences the properties of an electrospun material. The solution properties may be affected by additives as well, for instance, a surfactant possibly might reduce surface tension. When a solvent with a very low volatility is used, wet fibres are collected, i.e., the appearance of a film with pores rather than a fibre mat. However, if a solvent is too volatile, the Taylor cone solidifies suspending the production of a fibre. The variation of applied electrostatic potential and working distance also cause the variation of electric field strength. It was found that increasing electrostatic potential results in thinner fibres. Working distance, together with electrostatic potential determine the strength of an electric field. Working distance also changes a total flight time available to a fibre. Hence, in some cases increasing the working distance results in thinner fibres due to longer period of time for the bending instability (Fig. 2) to be developed and hence more time for the jet to be stretched. [4, 9]

All previously mentioned parameters influence the morphology of generated fibres. Morphology characterises the shape, diameter, topography of a single fibre surface, fibre association and the porosity of a structure. The morphology of a single fibre in literature is mostly described by scanning electron microscopy (SEM). Fibres formed during an electrospinning process are characterized by a diameter of 50–2000 nm. Dry fibres, that are uniform in morphology, generated by electrospinning technique in the narrow range of process parameters, are called a window process or a processing map. All parameters of a process have to be optimised to create beads-free uniform fibres (Figure 3). [10]

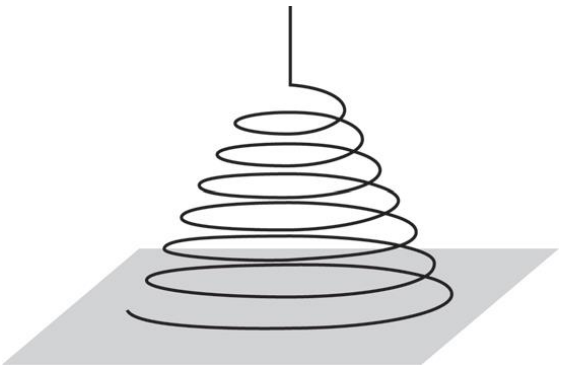

Figure 2. The typical representation of bending instability [4]

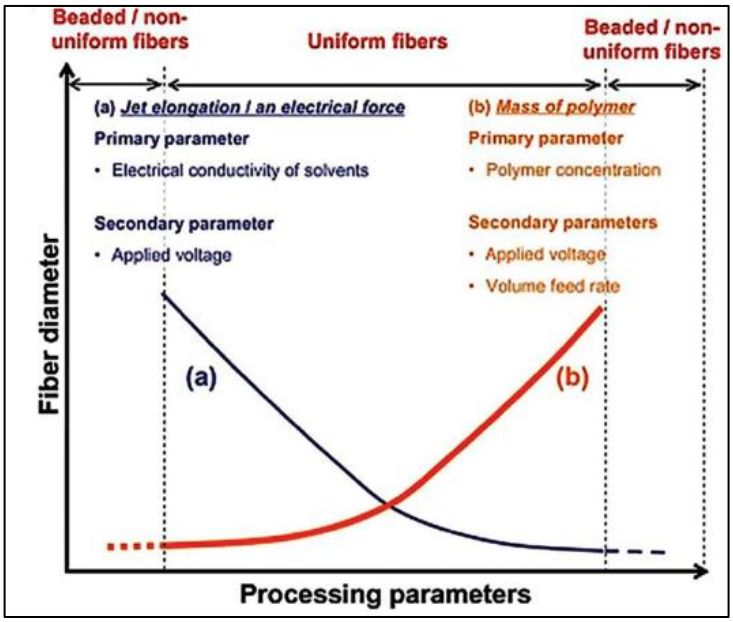


Figure 3. Fibres diameter as the function of parameters related to (a) forces in a solution jet and (b) polymer mass [11]

For the fabrication of nanofibers with desired properties, it is important to optimise the fulfilment of the electrospinning system. Due to the properties of nanofibers are affected by multiple system parameters coupled with each other, it is significant to be aware about relations between the electrospinning system and the system parameters, as shown in Table 2. Parameters that influence the performance are given in the order of priority. [12]

Table 2. Relations between the performance of an electrospinning system and the system parameters [12]

| **Performance** | **Parameters** |
|---|---|
| Spinnability | Solvent, concentration |
| Stability | Solvent, concentration, voltage and distance, feeding rate, humidity, temperature |
| Uniformity | Solvent, voltage, distance |
| Porosity | Solvent, humidity, temperature |
| Diameter | Concentration, voltage and distance |

### 1.1.2. Electrospinnable Polymers

Electrospun materials from nano/micro fibres can be produced using natural and synthetic polymers and required properties of these materials can be controlled by selecting polymers or its blends. More than 100 kinds of polymers can be used as base materials, including synthetic polymers as polyethylene oxide (PEO), polyacrylic acid (PAA), polylactic acid (PLA), polycaprolactone (PCL), polyurethane (PU), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) and polyacrylamide (PAM) as well as natural biobased materials, for instance, cellulose, cellulose acetate, collagen, gelatine, lecithin, chitosan, silk fibroin and hyaluronic acid. [5, 13]

Synthetic biopolymers as PCL and PLA are soluble in organic solvents while PVP and PVA are synthetic water-soluble biopolymers. Markedly, from many natural polymers, which have a low molecular weight and a relatively poor solubility, electrospinning into fibres is complicated without mixing them with synthetic polymers. Consequently, some synthetic polymers as PLA, PLGA, PCL, PVA and PEO are often co-electrospun with natural polymers as carrier ones. [14]

Due to the practicality, flexibility, mouldability, durability, chemical and physicochemical stability, natural polymers are preferable to synthetic ones. However, synthetic polymers often provide many advantages over natural polymers due to their easy adaptability according to desired properties for specific applications and they present good uniformity as well. Furthermore, synthetic polymers are more economical and served as more reliable source of raw materials than when considering source of natural polymers. [5, 13]

Most of the polymers are dissolved in solvents before electrospinning, as processing conditions involved are simple and direct. A polymer solution is obtained. In addition to this, some polymers may eject unpleasant or even harmful smells, thus a ventilation system is important to be installed. A few examples from the list of polymers which can be electrospun into nano/micro fibres and usable solvents are shown in Table 3. Instead of a solution, the polymer can be melted and supplied through a spinneret. In this case, a vacuum condition has to be applied. A few examples of polymer melts and their processing temperatures are shown in Table 4. [15]

Table 3. Polymers electrospun in solution form [15]

| No. | Polymer | Solvent |
|---|---|---|
| 1 | Nylon 6,6, PA-6,6 | Formic acid |
| 2 | Polyurethanes, PU | Dimethyl formamide |
| 3 | Polybenzimidazole, PBI | Dimethyl acetamide |
| 4 | Polyacrylonitrile, PAN | Dimethyl formamide |
| 5 | Polyvinyl alcohol, PVA | Distilled water |
| 6 | Polylactic acid, PLA | Dimethyl formamide |

The variety of soluble and fusible polymers (PVP, PU, PP, PVA, etc.) can be electrospun to form nano/micro fibres from their precursory solutions. Additionally, inorganic additives (e.g., $TiO_2$, ZnO) can be supplied into polymer solutions to form organic or inorganic composited nanofibers. Calcination at high temperature is introduced to decompose organic components thermally. Inorganic nanofibers can be received only with a slight morphological change. [16]

Table 4. Polymers eletrospun in melt form [15]

| No. | Polymer | Processing temp. (°C) |
|---|---|---|
| 1 | Polyethylene, PE | [200, 220] |
| 2 | Polypropylene, PP | [220, 240] |
| 3 | Polyethylene terephthalate, PET | 270 |
| 4 | Nylon 12, PA-12 | 220 |

## 1.2. The Main Types of Electrospinning Equipment and the Principles of their Working

1) Needle electrospinning

In the needle electrospinning (also called *nozzle electrospinning*) process a high voltage is required to conclude the electrically charged jet of a polymer solution or melt and solidify into a polymer fibre. The needle is connected to a high voltage supplier and the collector is grounded as it is shown in Figure 4. A polymer solution in syringe is applied to an electrical field. If the electrical force between the needle tip and the collector becomes stronger than the surface tension of a polymer solution, the charged jet of a fluid becomes as a Taylor cone. The needle goes through the small hole in a plate. This plate touches the needle thus a charge of a plate is given to the needle. Needle protrusion length is called the distance between the tip of the needle and the charged plate. This kind of electrospinning technique enables an incessant solution feeding and continuous electrospinning, the enclosed system avoids unnecessary evaporation and maintains solution stability, a fibre diameter is easily controlled. [17, 18]

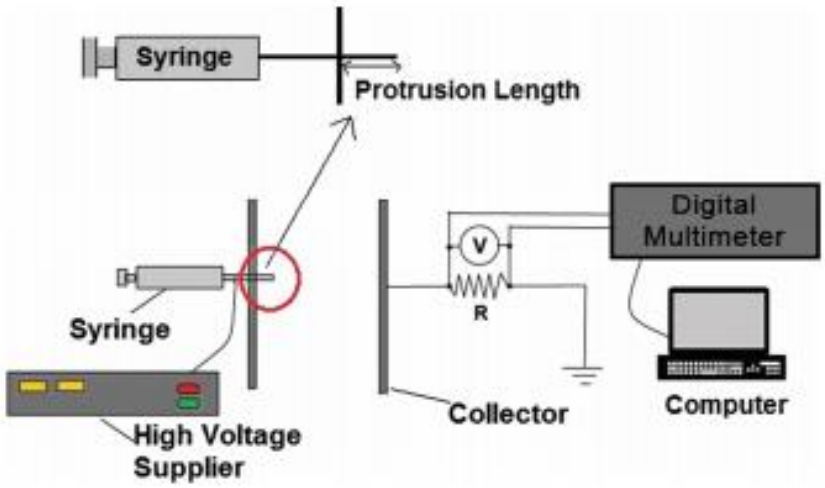


Figure 4. Needle electrospinning system [17]

With the desire of improving electrospinning productivity, the conventional needle electrospinning system can only produce a limited quantity of nanofibers and is not able to increase the demand of industrial applications and their magnitude. There is a solution regarding to forming a jet from a capillary tip, needleless electrospinning generated the large number of solution jets directly from an open liquid surface.

2) Rod electrospinning

In the rod electrospinning system, also called *stationary needleless electrospinning* (Fig. 5), the metal rod with 10 mm in diameter linked with high voltage supply is the spinning electrode. The collector is similar to the one used in needle electrospinning. The droplet of a polymer solution is placed at the upper end of the rod. Jets proceed on the surface of a droplet, close to its edge. This kind of electrospinning setup is relatively simple and electrospinning processes can be implemented with minimum efforts. Spinnerets in this category include a wire, a twisted wire, a conical wire, a bowl, a sharp edge, a cylinder, a slit, a curved slot, a stepped pyramid and a cleft (some examples are demonstrated in Figure 6). [17, 18]

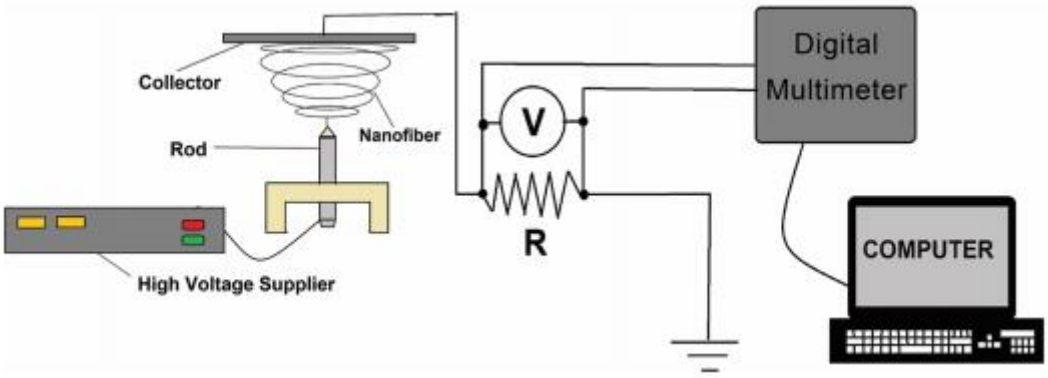


Figure 5. The illustration of rod electrospinning system [17]

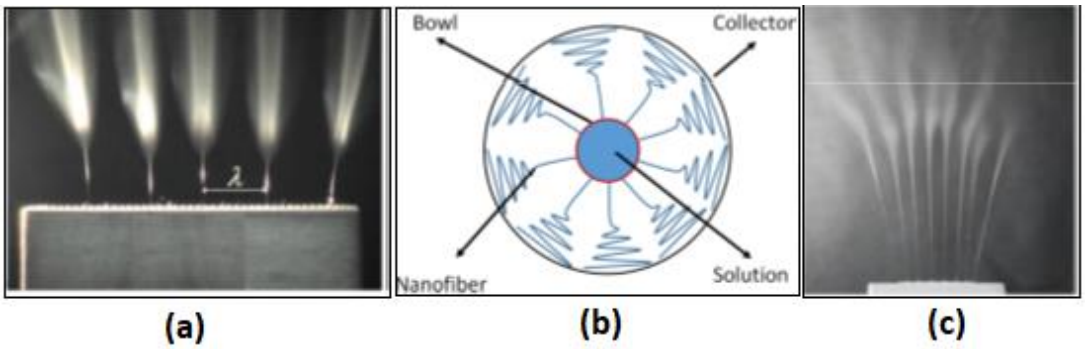


Figure 6. A few examples of the types of spinnerets: (a) cleft, (b) bowl, (c) slit [18]

3) Roller electrospinning

The roller electrospinning system (Figure 7) is another needleless process (also called *rotary electrospinning*) which is a highly productive method to produce nanofibers. The rotating roller placed in the solution tank is the spinning electrode. A supporting material (nonwoven web, paper, etc.) moves along the collector electrode. The roller electrospinning system is a closed system. There is only an input for air and humidity and output for air suction. In roller electrospinning much higher voltage is required than in needle electrospinning process. In addition, solution parameters as electrical conductivity and surface tension might have stronger influence on final electrospun material than in needle electrospinning due to process differences. [17, 19, 20]

When electrical force overcomes the surface tension of a polymer solution, many jets develop on the surface of the roller. A nanofiber layer covers the supporting material. The solution layer thickness can be easily regulated by the rotating speed with improved electrospinning stability and nanofiber

uniformity. Besides all electrospinning parameters as viscosity, polymer molecular weight, working distance, humidity. etc, the speed of the roller significantly influences the quality of the resultant nanofiber web (Figure 8). As a result, a continuous nanoweb is achieved. The roller electrospinning can process nano/micro fibres in the diameters of 50‑800 nm with acceptable narrow fibre diameter distribution on nonwoven webs. In addition, in roller electrospinning high voltage is required. [18, 19]

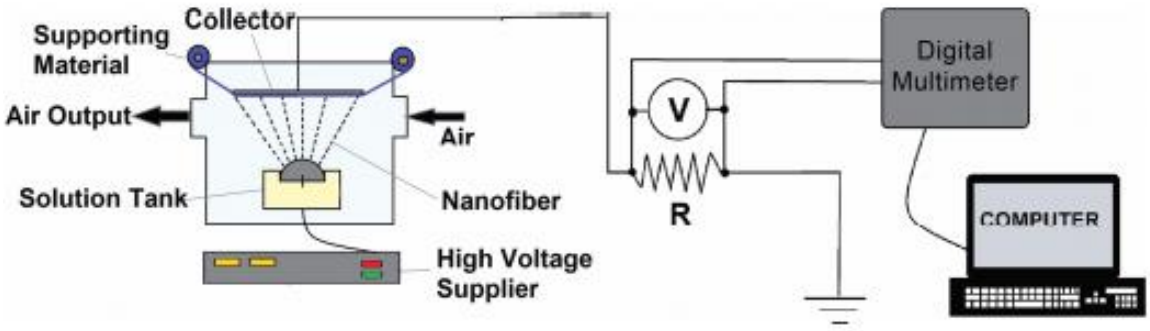


Figure 7. The illustration of a roller electrospinning system [17]

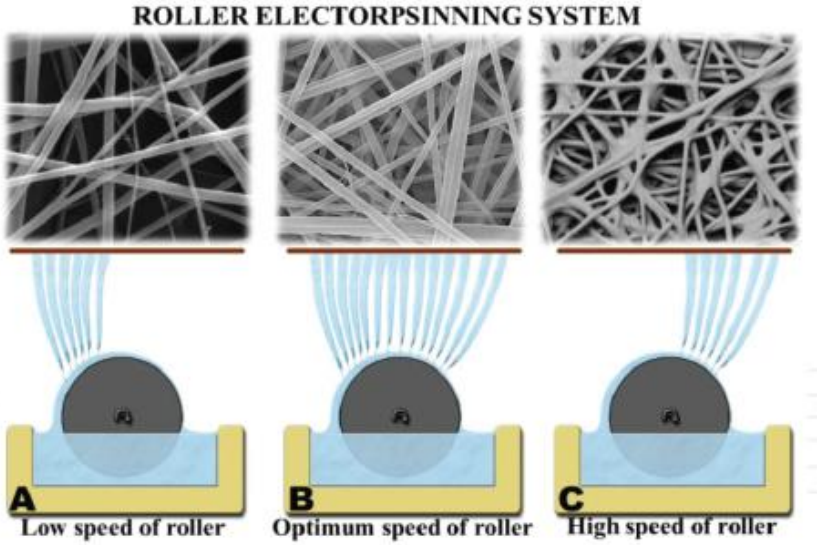


Figure 8. The effect of roller speeds on the quality of a nanofiber web [19]

### 1.3. The Application Fields of Nano/Micro Fibres Materials

All superior properties described before enhance the key role of electrospun nano/micro fibres as an ideal material candidate for a wide range of applications as biomedicine (e.g. tissue engineering, drug delivery, wound dressing and release control), filtration, reinforcement of composite materials, protective clothing, sound absorption, microelectronics (e.g. batteries, transistors, sensors and display devices) and space applications. Additionally, nano/micro fibres are applied in energy production and storage (photovoltaic cells and hydrogen storage), environmental protection and improvement, healthcare, sensors and many others. [5, 6, 7, 21]

### 1.3.1. Biomedical Field

One of the largest fields of nano/micro fibres is a biomedical one. Drug delivery is one of the most significant application. At the beginning of XXI century, researchers simply blended drugs with polymers to electrospin into drug-loaded fibre mats. For example, Kim et al. [22] successfully incorporated a hydrophilic antibiotic drug (Mefoxin, cefoxitin sodium) into a PLGA-based electrospun nanofiber mat to achieve the controlled release of drugs over the course of 1 hour. The results show that researchers observed no loss in structure or bioactivity.

In addition to the application of electrospun fibres in drug delivery systems, these materials are also widely used as scaffolds for tissue engineering due to their specific structural features. Continuous thin fibres created by electrospinning can mimic the ECM because of their large surface areas, ease of functionalization and complex fibrous interfacial topological structure. Generous studies on the application of electrospun nanofibrous scaffolds with various components for skin substitutes and wound dressings have been introduced. For example, Powell et al. [23] compared freeze-dried and electrospun collagen scaffolds as skin replacement and found that the electrospun scaffold skin substitutes possessed optimal cellular organization, potentially reducing wound contraction (Figure 9).

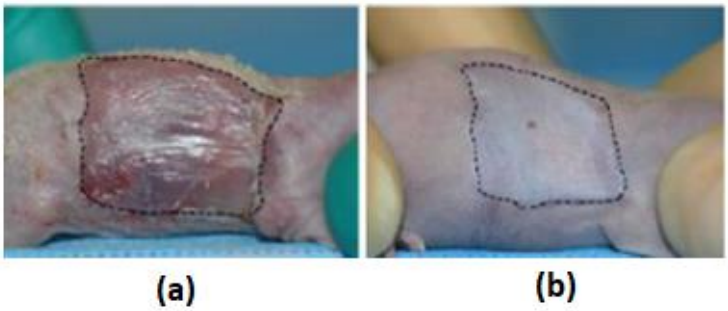


Figure 9. Electrospun nanofiber scaffold for skin regeneration; skin after (a) 2 weeks, (b) 8 weeks [23]

D. Archana et al. [24] developed a film from chitosan, PVP and silver oxide nanoparticles that showed improved results in regards of wound healing in comparison with research works had performed before. The outcome was good antibacterial activity and swelling capability what ensures no wound dehydration. The film was obtained transparent what makes checking of wound easy without removing it from the wound site. The macroscopic appearance is shown in Figure 10. At the day of surgery, no visible differences are visible with all different used materials. However, at the day 7, a primary tissue formation is observed clearly in chitosan and chitosan-PVP-silver oxide groups. At the day 14, wound closure is observed with the chitosan-PVP-silver oxide film. The prior effect was obtained due to the synergistic effect of constituents used.

Furthermore, humoral diagnosis of cancer can be fulfilled with nano/micro fibres materials. For instance, electrospun fibres were employed for the detection of tumour markers or circulating tumour cells (CTCs) in the blood and in other body fluids of a patient with early-stage cancer. Zhang et al. [16] generated titanium butoxide (TBT)/PVP composite fibres onto a silicon substrate. Titanium dioxide nanofibres were obtained by a calcination process and by removing organic components. Afterall, they modified the nanofibers with a biotinylated anti-epithelial cell adhesion molecule and finally were able to capture cancer cells.

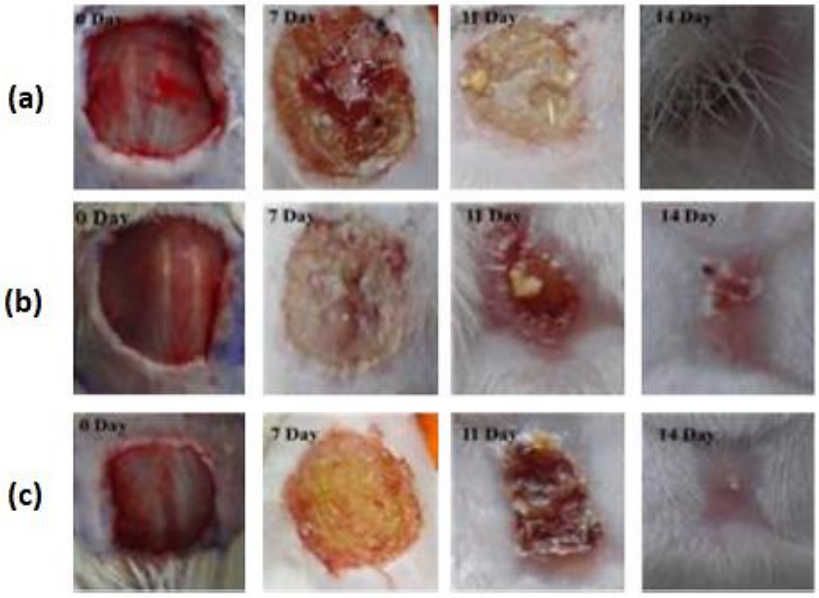


Figure 10. Macroscopic photographs of wounds contraction at 0th, 7th, 11th and 14th days after operation when using (a) gauze, (b) chitosan, (c) chitosan-PVP-silver oxide film [24]

### 1.4. Polyvinylpyrrolidone

Polyvinylpyrrolidone is known as a synthetic biomedical polymer. It is commonly called polyvidone or povidone, is a water-soluble polymer. PVP is obtained by free-radical polymerization from its monomer N-vinylpyrrolidone an initiator AIBN (azobisisobutyronitrile). PVP is an important amorphous polymer due to low chemical toxicity, high biocompatibility, excellent solubility in most organic solvents, good spinnability, and capability to interact with a wide range of hydrophilic materials. [25]

Dry PVP is a light flaky hygroscopic powder and can absorb up to 40% of water by its weight. In solution, it has excellent wetting properties and readily forms films which makes it good as a coating or an additive to coatings. [25]

PVP usage:

- as a blood plasma expander for trauma victims,
- as a binder in many pharmaceutical tablets which easily can pass through the body when it is administered orally,
- PVP added to iodine forms a complex called povidone-iodine (Betadine, Pyodine) that possesses disinfectant properties,
- as a constituent of wound dressings and drug delivery devices. [24, 25, 26]

#### 1.4.1. Electrospinning with PVP

There are many investigations established wherein PVP was used as an electrospun polymer to obtain nano/micro materials. PVP was solved in many solutions and their blends, for instance, water, methanol, ethanol, 50% ethanol/50% water, 2-propanol, 1,2-dichloroethane, chloroform and dichloromethane. SEM images of different cases are demonstrated in Figure 11. 8% PVP aqueous solution was tried to spin using needle electrospinning technique. Unfortunately, low quality of film was obtained with spherical beads and globs of PVP, possibly due to high surface tension of water

that created droplets from the solution. PVP has been solved with different constituents as well (silver nanoparticles, carbon nanotubes, titanium dioxide etc.) in order to receive certain properties, e.g. antibacterial, drug release, etc. [27, 28]

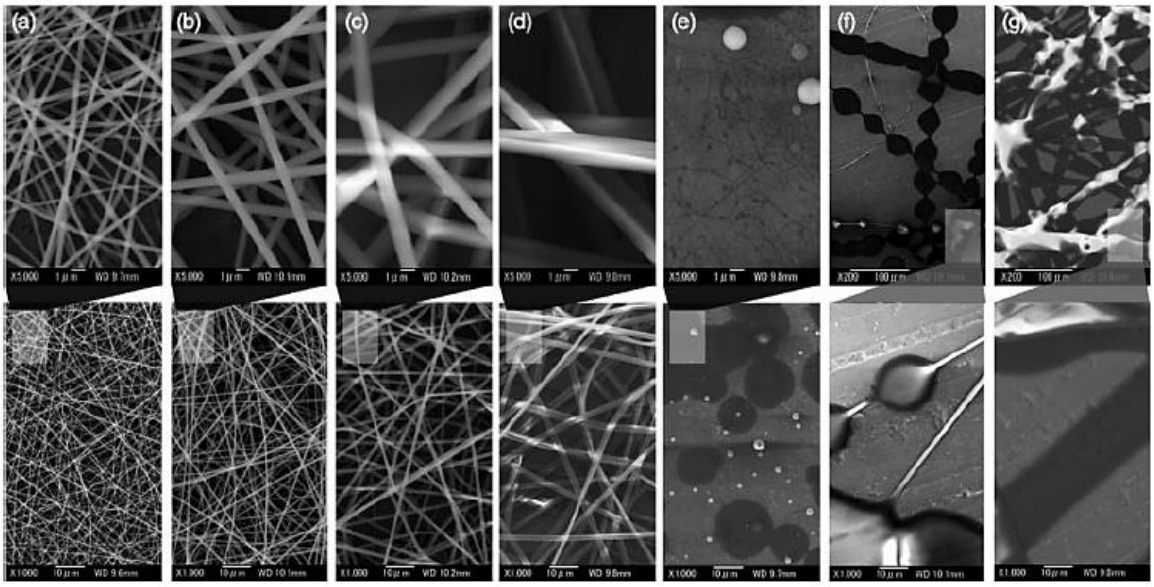


Figure 11. SEM images of the electrospun fibres from 8% PVP solutions in various solvents: (a) methanol, (b) ethanol, (c) 2-propanol, (d) DCE, (e) water, (f) chloroform and (g) DCM [27]

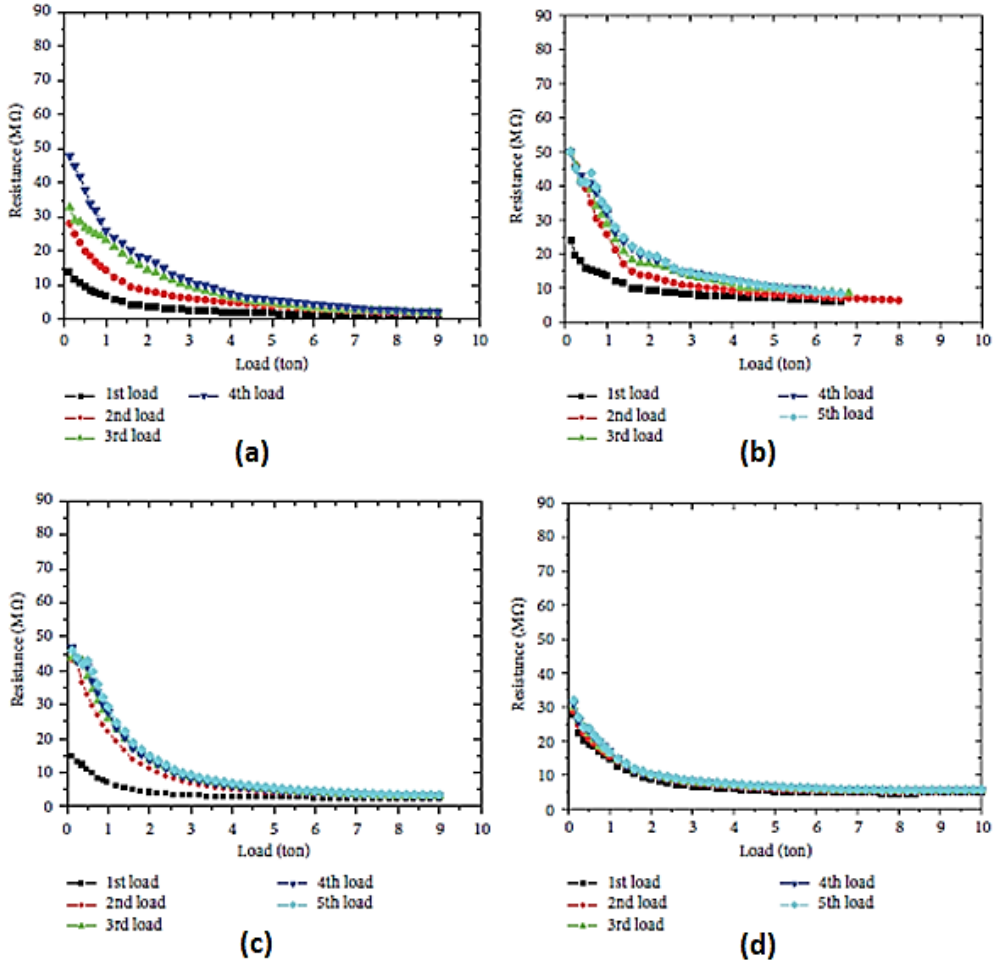


Figure 12. Load versus electrical resistance curves of PVP nanocomposite fibres obtained at following wt% MWCNTs: (a) 0, (b) 1, (c) 2, and (d) 4 [28]

Waseem S. Khan et al. [28] fabricated PVP nanocomposite fibres incorporated with multiwall carbon nanotubes (MWCNTs). The electrical resistance and some thermal properties of these nanocomposite fibres were determined. The significant test in this study (see Fig. 12) was loads versus the electrical resistance of PVP fibres. Values of the PVP nanocomposite fibres at various percentages of MWCNTs are demonstrated. As expected, resistance decreased with the applied load for all tested samples. Hence, at 0 wt% of MWCNTs (Figure 12 (a)), the resistance increased in each trial when the load was emitted. This might be explained by the hysteresis and porosity changes whereas at 1 and 2 wt% MWCNTs (Figures 12 (b) and (c)), the porosity of the fibre film reduced due to the conductive nanoscale insertions. Resistance increased only in the first trial after unloading, and in subsequent trials, in Figure 12 (d) the resistance curves overlapped due to the higher wt% of MWCNTs. Adding MWCNTs into the polymeric fibres increased both the thermal and electrical conductivities of fibres.

Rasekh et al. [26] demonstrated PVP – INDO (indomethacin) electrospun fibres in layering dressings. The superficial layer was produced by a single needle electrospinning technique in a single step. The XRD and DSC data showed that the drug existed in an amorphous state in the fibres. The complete release of the drug occurred within 45 min. Results confirmed that the fibres might be adjusted on any kind of dressing without varying their properties. Figure 13 exhibits the obvious difference between the wound dressing produced with conventional methods (fibre diameter ~30 μm) and made by electrospinning technique (~800 nm) that demonstrates a very high surface area ratio. Therefore, the electrospinning process potentially enables passive wound dressings to serve as active systems but still permitting any functionality of existing layers due to their porous and superficial nature.

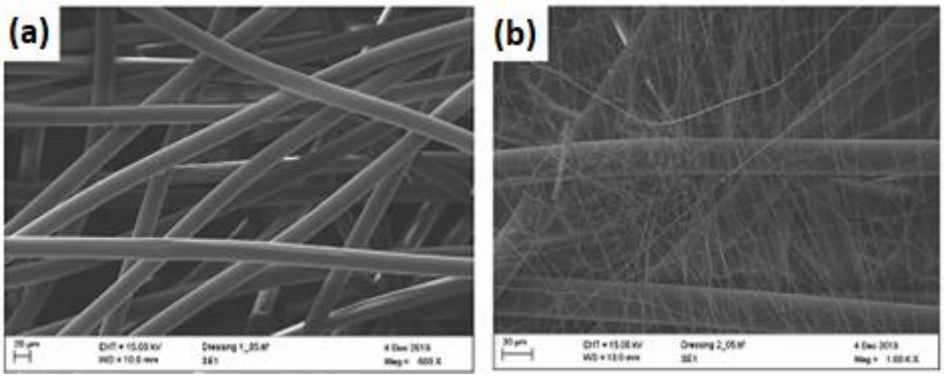


Figure 13. SEM images of wound dressings (a) without and (b) with PVP–INDO fibres [26]

E. Adomaviciute et al. [29] confirmed the possibility to introduce biological active compounds of propolis ethanolic extract into PVP mats by electrospinning. The product gave a successful outcome. It exhibited fast release of propolis phenolic compound that may be used in wound healing applications. In addition, colloidal solution with Ag NPs was added into a mixture that resulted in comparatively thinner nano/micro fibres formation. The inclusion of Ag NPs into spinning solutions demonstrated higher inhibition of many strains' growth compared with the case of only propolis phenolic compound.

### 1.5. Silver Nanoparticles

Since ancient times, silver is used as an antiseptic and antimicrobial agent against various bacteria and are increasingly used as an effective antibacterial agent for biomedical applications and wound

healing. Nanotechnology may be advantageous in treating bacterial infections. Further, the shapes of nanoparticles are an interesting field due to the variation in their effects on bacteria. [30, 31]

Hong et al. [32] compared the antibacterial activities of silver nano cubes, spheres and wires against *Escherichia coli* and found that spheres were more effective in the inactivation of *E. coli*. Further, it was concluded that the low specific surface area of silver nanowires was the probable reason for weakening of antibacterial activity. Due to the large effective specific surface area, the silver nano cubes and spheres had closer contact with bacterial cells and caused more damage to the bacterial cell membrane.

L. Sun and co-authors [33] investigated Ag NPs from $NaBH_4$ solution mixed with $AgNO_3$ and sodium citrate. A series of PVP coated Ag (Ag/PVP) nanoparticles with different morphologies were obtained with the addition of the different amount of PVP (Figure 14). It was evident that when the addition of PVP was 1,0 g, the shapes of the particles were mostly triangle and truncated triangular of the average particle size was 40-60 nm. When comparing Fig. 14 (a) and (c), it was concluded that the optimum addition amount of PVP was 1,0 g. Furthermore, the antibacterial test was accomplished for as-synthesized Ag/PVP nanoparticles. The results exhibited excellent antibacterial properties against *E. coli*, *S. aureus* and *P. aeruginosa*.

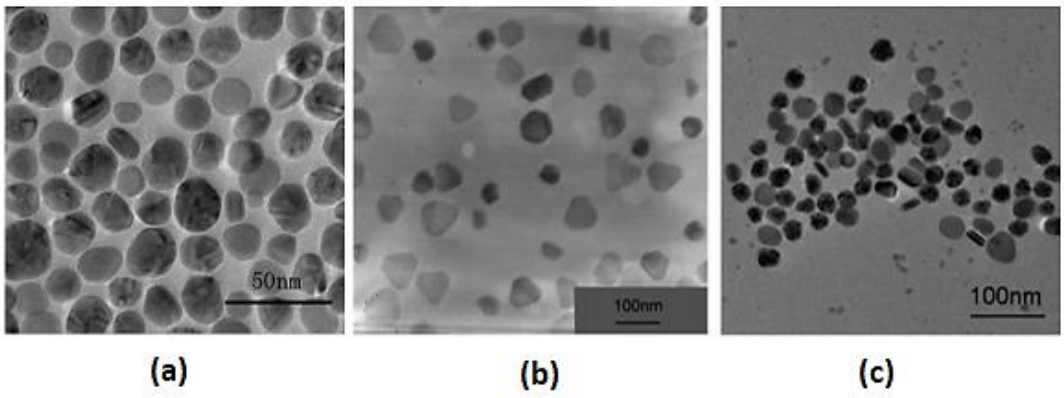


Figure 14. TEM images of Ag/PVP nanoparticles with different additional amount of PVP (a) 1,5 g, (b) 1,0 g and (c) 0,38 g [33]

Prokopovich and co-workers [34] investigated the noteworthy work of the antimicrobial activity of PMMA-based composite bone cement with the presence of Ag NPs. Ag NPs were used as a replacement of antibiotics in the development of an antibacterial bone cement. Antibiotic therapies are a time-limited solution because of the continuing increase of microorganisms' resistance to these molecules. Hence, scientist showed the alternative way to the reliance on antibiotics. They demonstrated the potential of developing antimicrobial bone cement through its impregnation with Ag NPs capped with oleic acid. Consequently, the high antimicrobial activity of bone cement was obtained against the most common source of post operatory infections meaning routinely antibiotics could be annulled. In addition, results proved there was no detrimental effect resulted from the presence of oleic acid capped Ag NPs on the mechanical properties of PMMA bone cement. Additionally, the cytocompatibility had no difference with the standard PMMA-based bone cement. It emphasised the benefit of the approach in preventing an infection offset in patients undergoing surgeries requiring bone cement.

It is proved that Ag NPs inhibit the formation of bacterial biofilms. The best example of a biofilm is a dental plaque that is bacteria that is formed on the surfaces of teeth. S. Mohanty et al. [35] stabilised Ag NPs with starch and indicated these Ag NPs may be used as antimicrobial agents against microorganisms. Scientists stated that Ag NPs exhibit potent antibacterial activity, besides being noncytotoxic to macrophages at the bactericidal concentrations, Ag NPs prevent biofilm formation and kill intracellular mycobacteria. For the observation of antibacterial activities *in vitro* conditions, the agar diffusion method was performed with exponentially growing *P. aeruginosa* (see Fig. 15). Incubation time was 24 hours. Starch alone was used as a reference wherein any inhibition zone was obtained. The inhibition zones of around 11 mm and 13 mm were observed by 1 μM and 2 μM Ag NPs, respectively, whereas the zone of 6 mm was formed by 2 μM $AgNO_3$ solution. It clearly showed the potent behaviour of Ag NPs on bacterial growth.

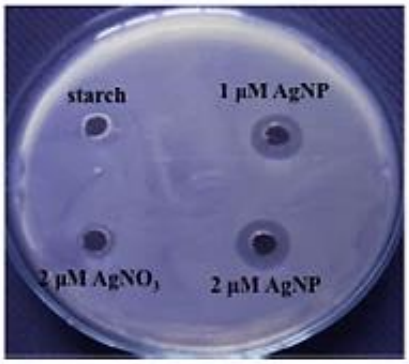


Figure 15. The antibacterial activity of Ag NPs performed by agar diffusion method [35]

Silver nanoparticles can be produced by various methods including biological, physical and chemical. Ag NPs are widely applied in nanomaterials while manufacturing healthcare and cosmetic products, antitumor drug carriers and antimicrobial and wound dressings. It is known that Ag NPs can affect the being of human cells. From *in vitro* cell testing, Ag NPs are reported to be toxic for variety of human cell lines, for instance, red blood cells, human keratinocytes, etc. However, the effect of Ag NPs on human cells depends on the size of particles, on their amount and the method of the production. Accordingly, it is important to immobilise Ag NPs into polymeric matrix to isolate them from the human cells. [36]

Polymer nanocomposites are applied in the medical fields to enhance wound healing. There is a typical example, Acticoat™ [37] dressing for burn care, a flexible polyethylene cloth coated with Ag NPs at a concentration between 0,69 and 1,64 mg/cm$^2$. Nanocrystalline silver is released to a wound are due to the surface plasmon resonance effect of silver. This avoids the use of toxic agents to fix colorants to the textiles. Due to the surface plasmon resonance effect of silver, Ag NPs can function as both, a colorant and antimicrobial agent for textile materials, thus toxic agents for the fixation of the colour of a textile is avoided.

Another example of Ag NPs application in nanocomposites is the research work accomplished by Oliveira et al. [38]. PVA/$AgNO_3$ nanocomposite hydrogels loaded with 0,25% and 0,5% $AgNO_3$ were produced. The findings showed a substantial inhibition against both gram-positive and gram-negative microorganisms due to the Ag+ ions released from $AgNO_3$. By the *in vivo* animal test, it was indicated that nanocomposite hydrogels containing Ag NPs are non-toxic.

### 1.5.1. Electrospinning with Silver Nanoparticles

Silver nanoparticles are highly demanded due to their superior antibacterial properties. Ag NPs are usually applied into electrospun solutions. G. Dong et al. [39] produced Ag NP embedded into PVP nanofibers by using a syringe pump in electrospinning technique. They tested an influence of heat treatment on nanofibers and Ag NPs. It was indicated that the biological activity of yeast cells was effectively inhibited, the diameter of nanofibers shrank and the size of Ag NP increased slightly. It is stated that those size-controlled Ag NPs embedded into polymer electrospun nanofibers can be used for antibacterial applications, catalysis, micro-electronics, sensors, etc.

Moreover, Wael Ali and co-authors [40] investigated composite carbon nanofibers that were prepared from Ag/PAN precursor by using needle electrospinning and heat treatment afterwards (Figure 16). UV absorption spectroscopy, SEMEDX and TEM demonstrated the production of Ag NPs with an average diameter of less than 4 nm. In addition, Ag NPs was found to be an effective means of improving the conductive performance of the carbon nanofibers. It can be used as a new innovative highly conductive electrode for many potential applications including lithium-ion batteries or supercapacitors with a more optimised carbon nanostructure. Subsequent study is supposed to be investigated in deeper insight into the underlying effects of heat treatment during stabilisation and carbonisation processes. Likewise, the effect of a nanoparticle size on morphology and properties of the composite should be considered.

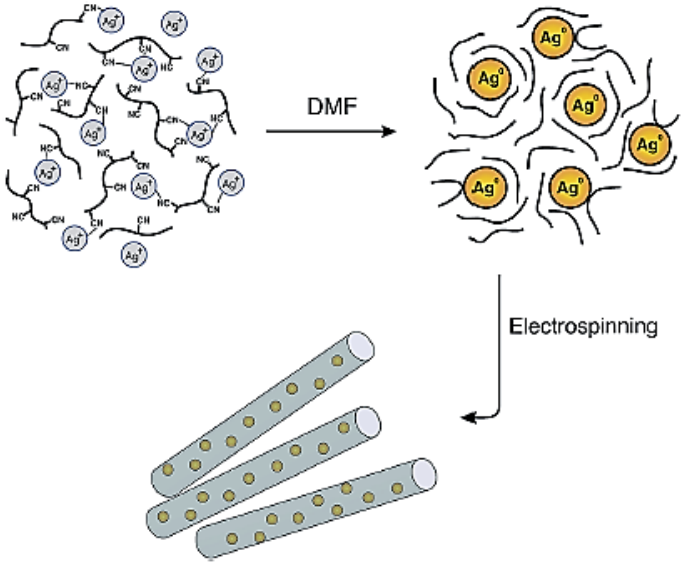


Figure 16. Schematic illustration of the production of composite nanofibers and the stability of Ag NPs by means of PAN after reduction via DMF [40]

Q. Shi et al. [41] prepared durable antibacterial Ag/PAN hybrid nanofibers by atmospheric plasma treatment and needle electrospinning method. Test results showed the uniform distribution of Ag NPs in nanofibers matrix. Antibacterial activity against both Gram-positive and Gram-negative microorganisms was received as excellent. Even the nanofiber mat was kept in aqueous solution, it still exhibited strong antibacterial activity. The potential applications of this product are in biotextiles, scaffolds, chemical/biological protection.

X. Jing et al. [42] formed ultrafine fibres from biodegradable PLA with Ag NPs via needle electrospinning process. They found the increase of fibre diameter with increasing amount of $AgNO_3$

added. Strong antibacterial activity was obtained due to Ag NPs. This follows into applications as wound dressing or anti-adhesion membranes.

Another study was performed by S. Pupkeviciute et al. [43]. PVA polymer with a small amount of colloidal Ag NPs were electrospun by needleless electrospinning technique. SEM images of six different compositions of nano/micro fibres are given in Figure 17. It can be seen that the addition of Ag NPs into the electrospun solution may led to formation of thinner nano/micro fibres. However, it was found that the inclusion of small amount of Ag NPs did not really influence the viscosity of solutions and the morphology of electrospun materials. Clearly, even the smallest amount of Ag NPs exhibited antibacterial property. Furthermore, FTIR analysis exhibited that colloidal Ag NPs in the polymer solution did not form any additional functional groups in antibacterial PVA electrospun material.

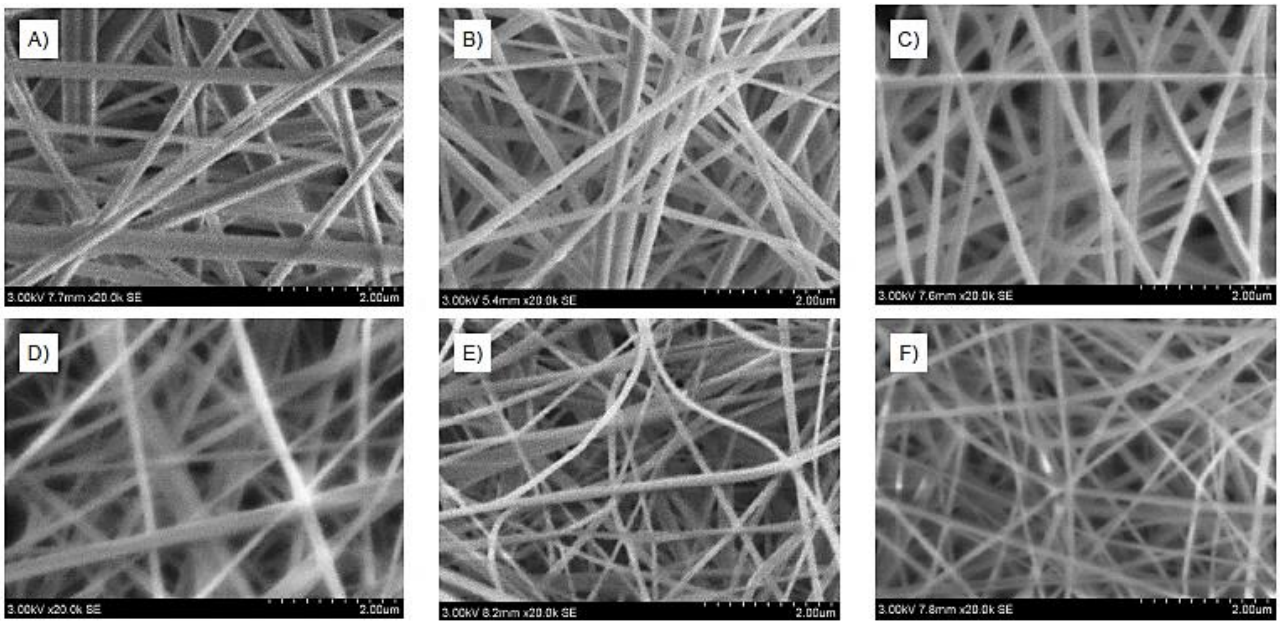


Figure 17. SEM images of electrospun PVA materials (scale 2 μm) with concentrations of (A) 15% PVA, (B) 15% PVA and 0,02% Ag NPs, (C) 15% PVA and 0,04% Ag NPs, (D) 11% PVA, (E) 11% PVA and 0,02% Ag NPs, (F) 11% PVA and 0,04% Ag NPs [43]

S. Huang et al. [44] produced PVP/cellulose nanocrystal (CNC)/Ag NPs composite fibres via electrospinning using N,N1-dimethylformamide (DMF) as a solvent. It was indicated that the PVP/CNC/Ag electrospun suspensions demonstrated 20% higher conductivity compared with those of the pure PVP solutions. Moreover, the average diameter of the PVP electrospun fibres decreased with the increase of the amount of CNCs and Ag NPs. It was attributed that a polymer solution was stretched due to the repulsion of the charges present on its surface, and more charges could be carried at higher solution conductivity, thus thinner fibres were formed.

Concerning wound dressing and care, another relevant study should be reviewed. Chitosan nanofibers containing various ratios of Ag NPs were obtained by I. K. Kwon and co-authors [45]. Chitosan is the second most abundant polysaccharide on earth and is an attractive natural polymer for biomedical use. The objective of this study was to fabricate pure chitosan nanofibers with Ag NPs with antibacterial efficacy in the zone of inhibition antibacterial test system. The schematic diagram of nanofiber production is presented in Figure 18. The results of this study demonstrated that the diameters were gradually decreased as the content of Ag NPs were increased. This may be explained

by the decrease of viscosity of the chitosan/Ag NPs electrospun solution upon an increase in the content of the chitosan/Ag NPs composite. This content as well was found to be affecting generation of fibre beads due to enhancement of surface tension of the electrospun solution. In antibacterial testing, the pure chitosan nanofibers did not inhibit bacterial growth while chitosan/Ag NPs nanofibers exhibited high degree of effectiveness against *P. aeruginosa* and *MRSA*.

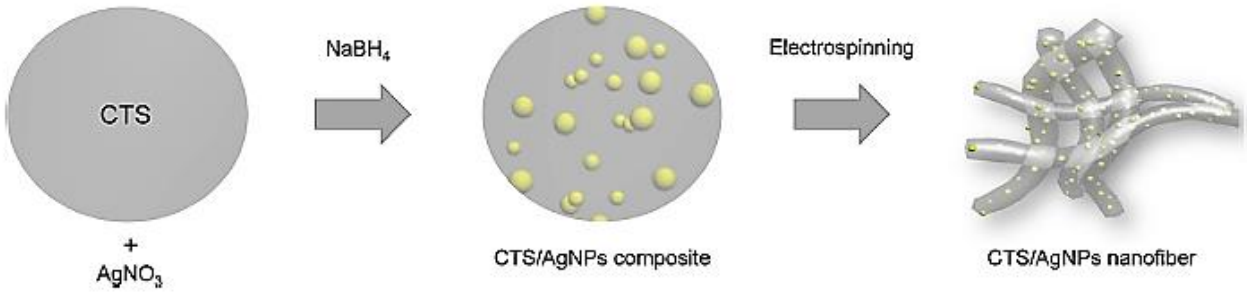


Figure 18. Schematic diagram of chitosan/Ag NPs nanofiber generation [44]

## 1.6. Conclusions of the Survey

To conclude the literature survey part, it is necessary to highlight that the process of electrospinning has conquered a lot of attention in the last decades due to a wide range of electrospinnable polymers, both natural and synthetic ones. Moreover, the electrospinning technique allows to consistently produce fibres in order to observe thinner or thicker nano/micro fibres depending on an application when changing certain parameters. It is one of the advantages as by using standard mechanical spinning technologies it is difficult to obtain submicron range products. With smaller pores and higher surface area than regular fibres, electrospun fibres have been successfully applied in various fields as biomedical, biotechnology, filtration, etc.

All preeminent parameters of electrospun fibres make them relevant in many advanced and everyday roles. However, the biomedical field is one of the biggest for nano/micro fibres applications. Drug delivery, scaffold production, wound healing and care, diagnosis of tumour cells are the examples wherein electrospun materials take an important place.

Two common methods can be operated for the production of nanofibers, needle electrospinning and needleless electrospinning. The morphology of formed structures on the collector using both methods varies with the parameters of a spinning device and process parameters. The needleless electrospinning system is a prior method for the industrial production. Comparing with the needle electrospinning system, the needleless one still has a high demand of further studies to be fulfilled. Polymer solution parameters, for instance, surface tension and viscosity, have higher influence in the needleless electrospinning than in the needle electrospinning technique.

In the literature a few studies were performed for the investigation of solution parameters and various process conditions which were tested to assess their effect on the morphology and the diameter of electrospun PVP nanofibers. Research works were focused on a fibre diameter rather than on the porosity of electrospun materials. Electrospun solutions were prepared from PVP polymers dissolving them in different solvents. However, nowadays the high interest is into the usage of green solvents. There was found a little number of studies wherein electrospun PVP solutions were aqueous. Finally, mostly research works were completed via needle electrospinning system.

Thus far, a lot of research works have been performed on the electrospun materials with silver nanoparticles using polymers, for example, polylactide, polyvinylpyrrolidone, polyvinyl alcohol, etc. In addition, commonly Ag NPs in electrospun solutions were obtained by the addition of ethanolic $AgNO_3$ solutions. The impact of the parameters of PVP/Ag NPs electrospun solutions on morphology and antibacterial properties of final nano/micro fibres have been a target of only a few studies. Despite that, most of the studies wherein it was analysed the influence of PVP polymer concentration and Ag NPs quantity on the structure and antibacterial activity of electrospun materials have been carried out by a needle electrospinning instead of the needleless roller electrospinning technique.

## 2. Methodology

### 2.1. Materials for Electrospun Solutions

Four substances were used for the production of electrospun solutions:

1) polyvinylpyrrolidone (PVP),
2) distilled water,
3) denatured ethanol,
4) 10 nm silver nanoparticles (Ag NPs) colloidal dispersion.

1) Polyvinylpyrrolidone (PVP) (linear formula $(C_6H_9NO)_n$), commonly used in medical applications due to the biobased polymer nature, was chosen for the formation of nano/micro fibres materials. PVP was supplied from Sigma-Aldrich (St. Louis, USA). The polymer is white colour powder of average molecular weight $M_w$ ~1300000 g/mol. Chemical structure is shown in Figure 19. [46]

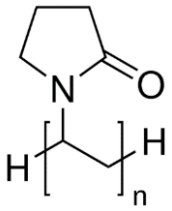


Figure 19. The chemical structure of polyvinylpyrrolidone [46]

3) Denatured ethanol >95 % (ethyl alcohol) (linear formula $C_2H_6O$) was selected as a solvent for this comparatively high molecular weight polymer in order to receive the proper structure of nonwoven materials.

4) Silver nanoparticles were chosen as an active substance due to its antibacterial properties. It can be applied and used as disinfectants and microbicides in many applications.

10 nm Ag NPs colloidal dispersion "RawAg" was provided from the company RhoNano (Vilnius, Lithuania). These Ag NPs are stabilised with the agent polyvinylpyrrolidone K30 ($M_w$ ~40000 g/mol) in water and ethanol. "RawAg" are produced by the new patented technology and are monodisperse with a narrow size distribution (see Fig. 20). These Ag NPs are produced in vacuum at clean conditions using high grade solutions. Technical specification of silver nanoparticles "RawAg" is given in Table 5. [47]

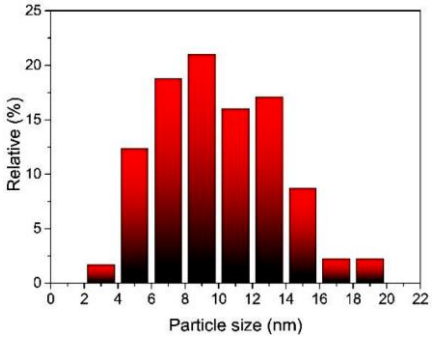


Figure 20. Size distribution of silver nanoparticles "RawAg" [47]

Table 5. Technical specification of silver nanoparticles “RawAg” [47]

| Characteristic | Value |
|---|---|
| Physical state | liquid |
| Colour | dark brown |
| Particle size | 10 nm |
| Size distribution (CV) | <30% |
| Concentration | 10000 ppm |
| Surface stabilization agent | PVP K30 |
| Purity of precursor (Ag) | 99,99% |
| Solvent | ethanol/ water |

## 2.2. Preparation of Solutions

The electrospinning solutions used for the fabrication of nano/micro fibres have been prepared by dissolving PVP polymer with the concentrations of 4%, 6% and 8% in distilled water. The aforementioned concentrations of PVP were prepared with ethanol afterwards. The concentrations of PVP were selected based on the other scientific works. [27, 43, 48] With each PVP concentration, solutions with 10 ppm, 50 ppm and 200 ppm Ag NPs were prepared by adding the certain amount of the 10 nm Ag NPs colloidal dispersion. The capacity of each solution was 220 ml. Solutions were stirred until solid particles were invisible and left for 24 hours at room temperature (Fig. 21). The percentage composition of prepared electrospun solutions is adduced in Table 6.

Table 6. Composition of electrospun solutions

| No. | Composition of an electrospun solution | Content of pure Ag NPs in a solution, ppm | Content of pure Ag NPs in a solution, % |
|---|---|---|---|
| 1’ | 4% PVP + 96% $H_2O$ | - | - |
| 2’ | 6% PVP + 94% $H_2O$ | - | - |
| 3’ | 8% PVP + 92% $H_2O$ | - | - |
| 1 | 4% PVP + 96% $C_2H_50H$ | - | - |
| 2 | 4% PVP + 95,9% $C_2H_50H$ + 0,1% 10 nm Ag NPs colloidal dispersion | 10 | 0,001 |
| 3 | 4% PVP + 95,5% $C_2H_50H$ + 0,5% 10 nm Ag NPs colloidal dispersion | 50 | 0,005 |
| 4 | 4% PVP + 94% $C_2H_50H$ + 2% 10 nm Ag NPs colloidal dispersion | 200 | 0,02 |
| 5 | 6% PVP + 94% $C_2H_50H$ | - | - |
| 6 | 6% PVP + 93,9% $C_2H_50H$ + 0,1% 10 nm Ag NPs colloidal dispersion | 10 | 0,001 |
| 7 | 6% PVP + 93,5% $C_2H_50H$ + 0,5% 10 nm Ag NPs colloidal dispersion | 50 | 0,005 |
| 8 | 6% PVP + 92% $C_2H_50H$ + 2% 10 nm Ag NPs colloidal dispersion | 200 | 0,02 |
| 9 | 8% PVP + 92% $C_2H_50H$ | - | - |
| 10 | 8% PVP + 91,9% $C_2H_50H$ + 0,1% 10 nm Ag NPs colloidal dispersion | 10 ppm | 0,001 |

| No. | Composition of an electrospun solution | Content of pure Ag NPs in a solution, ppm | Content of pure Ag NPs in a solution, % |
|---|---|---|---|
| 11 | 8% PVP + 91,5% $C_2H_50H$ + 0,5% 10 nm Ag NPs colloidal dispersion | 50 ppm | 0,005 |
| 12 | 8% PVP + 90% $C_2H_50H$ + 2% 10 nm Ag NPs colloidal dispersion | 200 ppm | 0,02 |

Figure 21. Preparation of solutions

## 2.3. Determination of the Viscosity of Electrospun Solutions

Viscosity measurements were carried out by operating the rotational viscometer Brookfield DV-II+PRO (Brookfield Engineering Laboratories, Inc., US) (Figure 22) which enables to measure fluid viscosity in the range of rotational speed from 0,1 rpm up to 200 rpm. Accordingly, 120 rpm were applied for the measurements. Five measurements were taken for each solution. The measurement tool was used standard spindle *LV2* immersed in the test fluid through a calibrated torsion spring. Test were fulfilled in Faculty of Mechanical Engineering and Design (Kaunas University of Technology). [49]


Figure 22. The viscometer The Brookfield DV-II+Pro (Brookfield Engineering Laboratories, Inc., US)

## 2.4. Determination of the Surface Tension of Electrospun Solutions

The multifunctional dynamic contact angle measuring device and tensiometer DCAT 21 (DataPhysics Instruments GmbH, Germany) (Figure 23) was operated for the measurement of the dynamic surface tension of solutions. Tests were accomplished in Faculty of Mechanical Engineering and Design (KTU). Wilhelmy Plate method was applied (Figure 24). It employs a microroughened

platinum iridium plate (19,90 mm in width and 0,20 mm in thickness) attached to a microbalance. The surface tension measurements were based on weight determination. [50, 51]

In this technique the plate is detained at the interface and held in this position by a force that maintains a balance between the plate and the meniscus force of the liquid. The force is proportional to the interfacial tension as described by:

$$\gamma_l = \frac{F}{p \cdot \cos\theta} \quad (1)$$

Figure 23. Dynamic contact angle measuring devices and tensiometer DCAT 21 (DataPhysics Instruments GmbH, Germany)

where $F$ is force measured by using a microbalance, $p$ is perimeter of the three-phase contact line $l \cdot L_w$, $\theta$ is the contact angle measured for the liquid meniscus in contact with the object surface. Repeated cycles of immersion and emersion were performed at a rate of 1 mm/s. Immersion depth of the plate was d = 3 mm. Five measurements were taken for each solution. [50, 51]

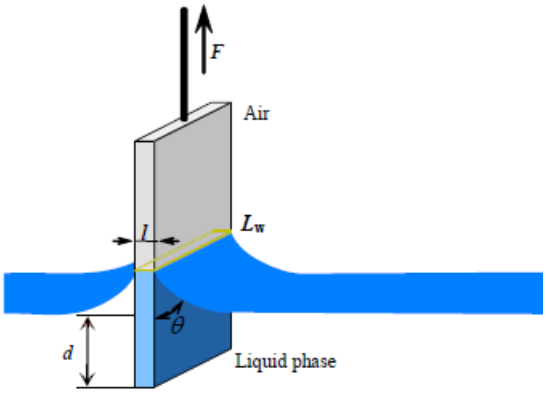


Figure 24. Schematic representation of Wilhelmy plate method [51]

## 2.5. Determination of the Conductivity of Electrospun Solutions

The conductivity of ethanolic solutions were measured by EcoSense EC300 conductivity meter (YSI Life Sciences, USA) (Figure 25) in Institute of Chemistry, Faculty of Chemistry and Geoscience (Vilnius University). An electrical conductivity probe was immersed in a solution, held for 5 minutes for a value to be settled down. Five measurements were taken for each solution. [52]


Figure 25. EcoSense EC300 conductivity meter (YSI Life Sciences, USA) [52]

## 2.6. Formation of Electrospun Nonwoven Materials from Nano/Micro Fibres Using "Nanospider™"

Formation of PVP nano/micro fibres was accomplished by using the needleless roller electrospinning equipment "Nanospider™" (Elmarco, Czech Republic) (Figure 26) in Faculty of Mechanical Engineering and Design (KTU).


Figure 26. (a) – "Nanospider™" (Elmarco, Czech Republic), (b) – work environment and setup

"Nanospider™" operates as a modified electrospinning method which requires the use of a high voltage electrostatic field to create the electrically charged stream of a polymer solution. The technique is based on the production of nanofibers from the thin layer of liquid polymer (or melt). Hereby, Taylor cones (the source of nanofiber) are obtained on the surface of the lower roller spinning electrode with tines (Figure 27) which is partially immersed in the tank with polymer solution (illustrated in Figure 27). A grounded collector electrode is placed at the top of the spinner and an antistatic substrate is below and collects flying nano/micro fibres. When the applied electrical field between the roller and the ground electrodes exceeds the surface tension of the electrospinning

solution, the solution jets are formed, and the nano/micro fibres are produced during their flight from the roller to the ground electrode. The solvent (water, ethanol, etc.) is evaporated during this flight time between the roller and the ground electrodes. Set up parameters for electrospinning process are adduced in Table 7. [53, 54]

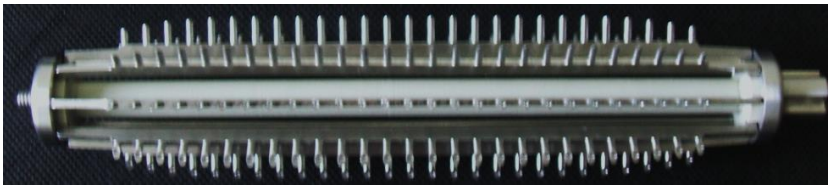

Figure 27. The lower roller spinning electrode with tines

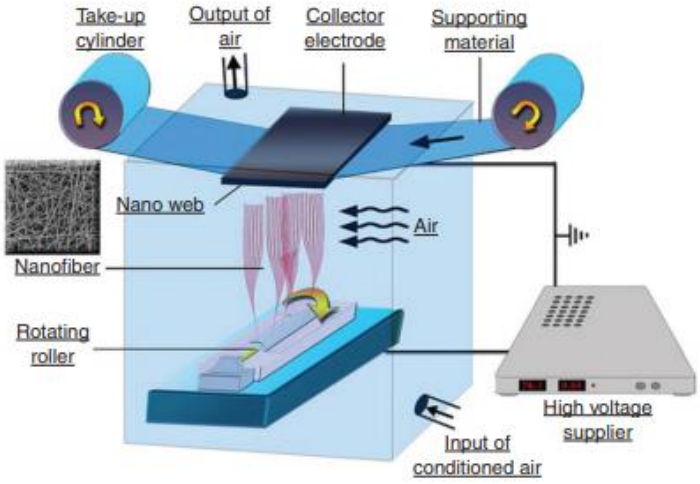


Figure 28. Set up of "Nanospider$^{TM}$" equipment [54]

Table 7. Constant parameters of electrospinning process

| **Parameter/ characteristic** | **Value** |
|---|---|
| Temperature *T*, ºC | 20 ± 2 |
| Relative humidity *RH*, % | 42 ± 4 |
| Voltage *V*, kV | 60 ± 0,2 |
| Roller speed *v*, rpm | 6 |
| Working distance *L*, cm | 13 |
| Time *t*, min | 7 |
| Supporting material | PP |

## 2.7. Determination of the Structure of Electrospun Nonwoven Materials (SEM Analysis)

The morphology analysis of nano/micro fibres were performed by Scanning Electron Microscope Model S-3400N (Hitachi High-Technologies, Japan) (Figure 29) in Lithuanian Energy Institute. SEM images were generated at magnifications: ×500 when scale was 100 μm, ×1000 when scale was 50 μm, ×5000 when scale was 10 μm and ×10000 when scale was 5 μm. SEM scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition. [55]


Figure 29. Scanning Electron Microscope Model S-3400N (Hitachi High-Technologies, Japan) [56]

## 2.8. Method of the Diameter Measurement of Nano/Micro Fibres (Software NIS-Elements)

The investigation of nano/micro fibres diameter was performed by using software NIS-Elements (Nikon Corporation, Japan). For each sample (in total 12 samples) 100 fibres' diameters were measured from at least 3 SEM images. Work environment is demonstrated in Figure 30. Obtained values of nano/micro fibres diameter were employed in generating diagrams and counting mean values by Microsoft Excel 2019.

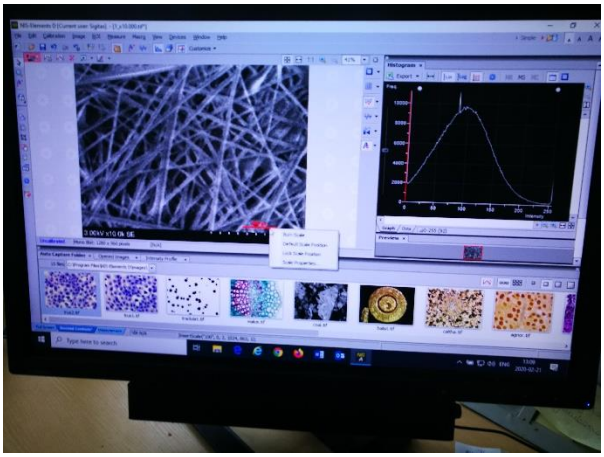

Figure 30. Work environment of software NIS-Elements (Nikon Corporation, Japan)

## 2.9. Determination of Porosity (Gravimetric Method)

Porosity is a significant parameter of all textile materials. It can be defined as a ratio of void volume in total volume of a material. In other words, it is a quality of being porous. Typical porosity values for electrospun materials are in the range [70–95] %. There are different techniques to measure it. Gravimetric determination was an attractive one due to available equipment in the laboratory. Optical microscope Nikon E200-F (Figure 31) were carried out for the measurement of the thickness of electrospun materials (Figure 32) and a laboratory scale to weigh it. [57, 58]

Figure 31. Optical microscope Nikon E200-F [57]

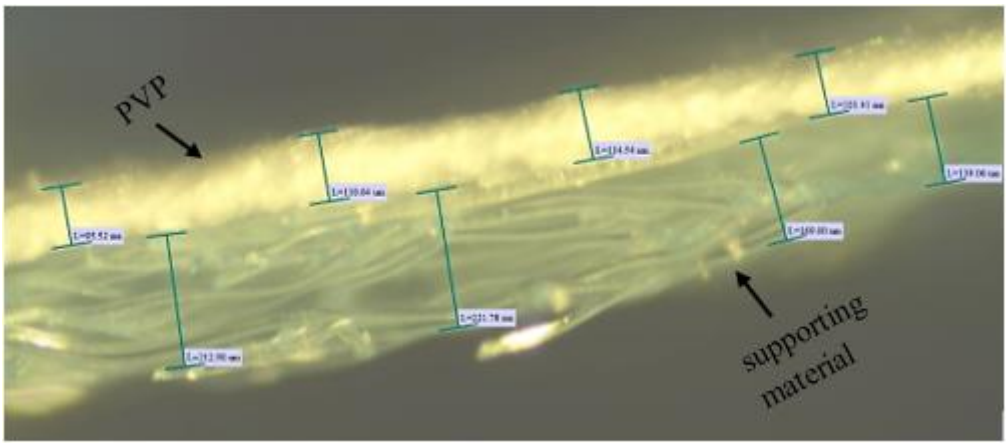


Figure 32. Image, generated by optical microscope Nikon, exhibits the thickness measurement of an electrospun material

The electrospun mat porosity P was determined via density of the electrospun material $\rho_m$ and density of the bulk material $\rho_b$ according to the formula [59]:

$$P = \left(1 - \frac{\rho_m}{\rho_b}\right) \cdot 100\% \quad (2)$$

Bulk material density is known as a constant $\rho_b(PVP) = 1{,}2\ g/cm^3$. Density of Ag NPs was not considered due to extremely low concentration in a solution. Density of electrospun material was calculated:

$$\rho_m = \frac{m}{h \cdot a} \quad (3)$$

where *m* is mass, *h* – thickness, measured by optical microscope and *a* – area of the sample. Thickness measurement was taken 4 times in 3 different places of the sample (12 measurements for each sample). Average porosity value was calculated. [59]

### 2.10. Detection of Silver Nanoparticles (EDS Analysis)

Energy dispersive X-ray spectroscopy (EDS, EDX) was selected as a method to detect silver nanoparticles on the surface of electrospun materials. Bruker Quantax 800 equipment was used to obtain spectra of elements. Analysis were accomplished in Lithuanian Energy Institute.

EDS is a standard method for identifying and quantifying elemental compositions in the very small sample of a material (even a few cubic micrometres). The EDS apparatus contains four basic components: the excitative source (electron beam or X-ray beam), the X-ray detector, the pulse processor, and the analyser. To stimulate the emission, the high-energy beam of charged particles such as electrons or protons, or the beam of X-rays, is focused into the observable specimen. [56]

## 2.11. Determination of the Antibacterial Activity of Electrospun Materials (Kirby-Bauer Disk Diffusion Method)

The Kirby-Bauer test was carried out in Hospital of Lithuanian University of Health Sciences Kaunas Clinics for produced electrospun materials to find out whether they inhibit bacteria growth. This test is known as the disk-diffusion method used for antibiotic susceptibility test for determination of antibiotics type when treating a certain infection. This method relies on the inhibition of bacterial growth measured under standard conditions. Illustration of the method is shown in Figure 33. An agar plate is first spread with bacteria, then paper disks of antibiotics are added. The bacteria start growing on the agar media. The amount of space around every antibiotic plate indicates the lethality of that antibiotic on the bacteria in question. Highly effective antibiotics (disk C) will produce a wide ring of no bacterial growth, while an ineffective antibiotic (disk A) will show no change in the surrounding bacterial concentration at all. The effectiveness of intermediate antibiotics (disk B) can be measured using their zone of inhibition. [60, 61]

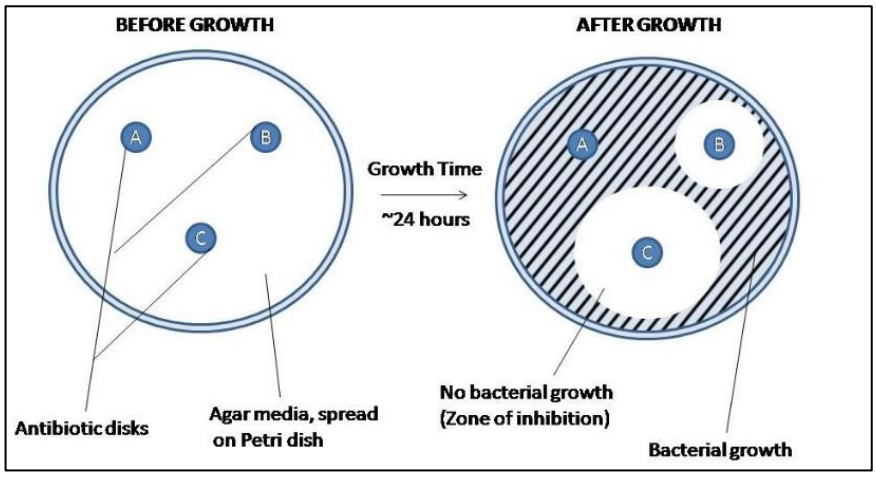


Figure 33. Kirby-Bauer test (disk diffusion method) [61]

To investigate the mechanism of the inhibition zone on microorganisms, two strains of bacteria, namely Gram-negative *Escherichia coli (E. coli)* and Gram-positive *Staphylococcus aureus (S. aureus)* were presented. The organism grows on the agar plate while Ag NPs (the antibiotic) is supposed to inhibit the growth. If the organism is susceptible to a specific antibiotic, there is no growth around the disc containing the antibiotic. Thus, the zone of inhibition is observed and measured to determine the susceptibility to an antibiotic for that organism. [60, 62]

## 2.12. Statistical measures

Statistical measures were used to describe the average of the results and their spread as usually textile testing contains the set of repeated measurements.

Arithmetic mean or average value was calculated [63]:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \quad (4)$$

standard deviation was calculated [63]:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (x_1 - \bar{x})^2}{n-1}} \quad (5)$$

coefficient of variation was calculated [63]:

$$CV = \frac{SD}{\bar{x}} \cdot 100\% \quad (6)$$

standard error was calculated [64]:

$$SE = \frac{t_{0,95} \cdot SD}{\sqrt{n}} \quad (7)$$

where $x$ – individual value of the variable, $n$ – number of individuals, $t_{0,95}$ – Student value when confidence level is 0,95.

## 3. Results and Discussions

According to the targeted objectives, the results were obtained by different experimental techniques and compared to each other. The findings and discussions are presented in the following sections.

### 3.1. Formation of Nano/Micro Fibres from Aqueous and Ethanolic PVP Solutions

In the first part of the experimental work, aqueous and ethanolic solutions with 4%, 6% and 8% PVP concentrations were prepared. It has been reported that the electrospinnability and the morphology of formed fibre depend on solution parameters, for example, the surface tension and the viscosity of a solution. Those important parameters were tested and are shown in Table 8. [10]

Table 8. Surface tension and viscosity of aqueous and ethanolic electrospun solutions

| **Composition of an electrospun solution** | **Surface tension $\gamma \pm SE$, mN/m** | **Viscosity $\eta \pm SE$, mPa·s** |
|---|---|---|
| 4% PVP + 96% $H_2O$ | 66,36 ± 0,30 | 96 ± 11 |
| 6% PVP + 94% $H_2O$ | 65,09 ± 0,19 | 155 ± 15 |
| 8% PVP + 92% $H_2O$ | 63,02 ± 0,17 | 297 ± 15 |
| 4% PVP + 96% $C_2H_6O$ | 23,09 ± 0,27 | 104 ± 11 |
| 6% PVP + 94% $C_2H_6O$ | 22,54 ± 0,19 | 170 ± 15 |
| 8% PVP + 92% $C_2H_6O$ | 21,64 ± 0,19 | 325 ± 18 |

According to obtained data (Table 8), it can be stated that the surface tension of aqueous solution is almost 3 times higher than ethanolic one, meaning in water molecules are attracted 3 times stronger to each other. In both cases, ethanolic and aqueous solutions, the surface tension decreased gradually when the polymer concentration increased.

In addition, the viscosity of prepared electrospun solutions was tested. In Table 8, obviously, with the increase of polymer concentration, viscosity increased as well. For example, the viscosity of the ethanolic 4% PVP solution was $\eta$ = 104 ± 11 mPa·s when viscosity of the ethanolic 6% PVP solution was $\eta$ = 170 ± 15 mPa·s. In the same context, a little change might be noticed when comparing aqueous and ethanolic solutions with the same amount of PVP. For instance, the viscosity of the aqueous 8% PVP solution was $\eta$ = 297 ± 15 mPa·s while the viscosity of the ethanolic 8% PVP solution was $\eta$ = 325 ± 18 mPa·s.

At the first stage, these six solutions of pure PVP described above were electrospun by using Elmarco equipment "Nanospider$^{TM}$" (Czech Republic). Thus, prepared solutions were carried out by immersing them to the tank. There were parameters set up as constant (selected based on other scientific works [48, 65]): working distance $L$ = 13 cm, applied voltage $V$ = 60 ± 0,2 kV, roller speed $v$ = 6 rpm and the time of electrospinning process of each sample $t$ = 7 min.

In regard to other trials made until now, the desire was to generate nano/micro fibres from PVP aqueous solution. S. Yoshikawa et al. [27] attempted to spin 8% PVP aqueous solution using needle electrospinning technique. Unfortunately, low quality of film was obtained with spherical beads and globs of electrospun PVP material. As a result of the needleless roller electrospinning technique, from 4% and 6% PVP aqueous solutions, Tailor cones were generated visibly, and electric current was presented in the range [0,020, 0,044] by "Nanospider$^{TM}$". However, SEM photographs demonstrated

that fibres material was not created. Only the film attached to the supporting material was achieved (see Figure 34). Unsuccessfully, electrospinning from the solution of 8% polymer concentration was not processed. The problems might be caused due to extremely high surface tension and high dielectric constant of water. Thus, a further study could be proposed to mix water with a solvent that has lower surface tension in terms of reducing surface tension of an electrospun solution.

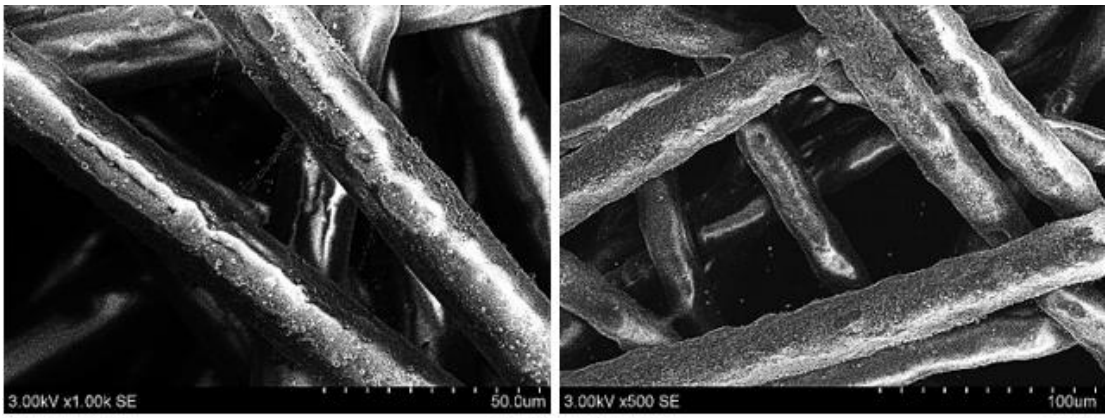


Figure 34. SEM images of electrospun materials from (a) 4% (magnification ×1000, scale 50 $\mu$m), (b) 6% PVP aqueous solutions (magnification ×500, scale 100 $\mu$m)

Furthermore, the electrospun materials from 4%, 6% and 8% PVP ethanolic solutions were formed successfully. All set up parameters were used as mentioned before with the aqueous case. SEM images are given in Figure 35. Generally, the obtained nano/micro fibres can be claimed as quite uniform and smooth however a couple of defects were found. It was detected the electrospun 4% PVP material had beads in the structure (see Fig. 35 (1)) and the 8% PVP material had a bundle of stuck fibres (see Fig. 35 (2)). The formation of beads are closely correlated to the viscoelastic jet break-up theory. It has been constituted that the formation of beads is interacted with the viscoelasticity of a solution. [66]

With the increased polymer concentration, beaded-free fibres were obtained (from 6% and 8% PVP solutions) due to presenting more highly extensible compounds (PVP polymer) into the precursor solution. Certainly, as other scientific works had been proved, it is seen that a higher concentration solution has a higher viscosity, thus it leads to the formation of thicker fibres. This is due to the high polymer concentration solution which has less solvent to evaporate and takes less time to solidify. Evidently, from 6% PVP solution (Fig. 35 (c)) nano/micro fibres were thinner than the ones of 8% PVP solution (Fig. 35 (b)) but thicker than 4% PVP (Fig. 35 (a)). [11, 51, 54]

Moreover, in Figure 36 the data showed the same tendency as SEM images in terms of polymer concentration influence on a fibre diameter. The polymer concentration increase led to thicker nano/micro fibres. For example, the diameters of the 4% PVP fibres were up to 200 nm in 80% cases while the diameters of 6% PVP fibres were up to 200 nm in 59% cases and consequently from 8% PVP solution, 45% cases were achieved up to 200 nm.

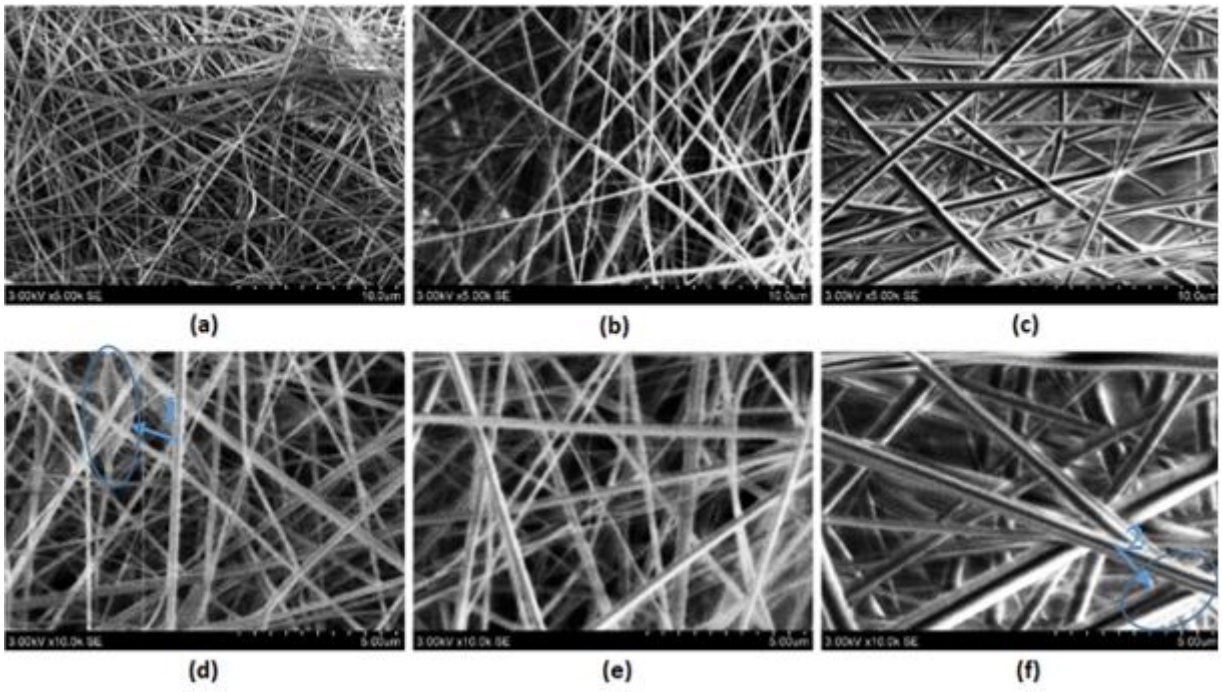


Figure 35. SEM images of PVP nano/micro fibres from ethanolic solutions of (a) 4%, (b) 6%, (c) 8% PVP concentration (magnification ×5000, scale 10 $\mu$m) and (d) 4%, (e) 6%, (f) 8% PVP concentration (magnification ×10000, scale 5 $\mu$m); 1 – a bead, 2 – a bundle of stuck fibres

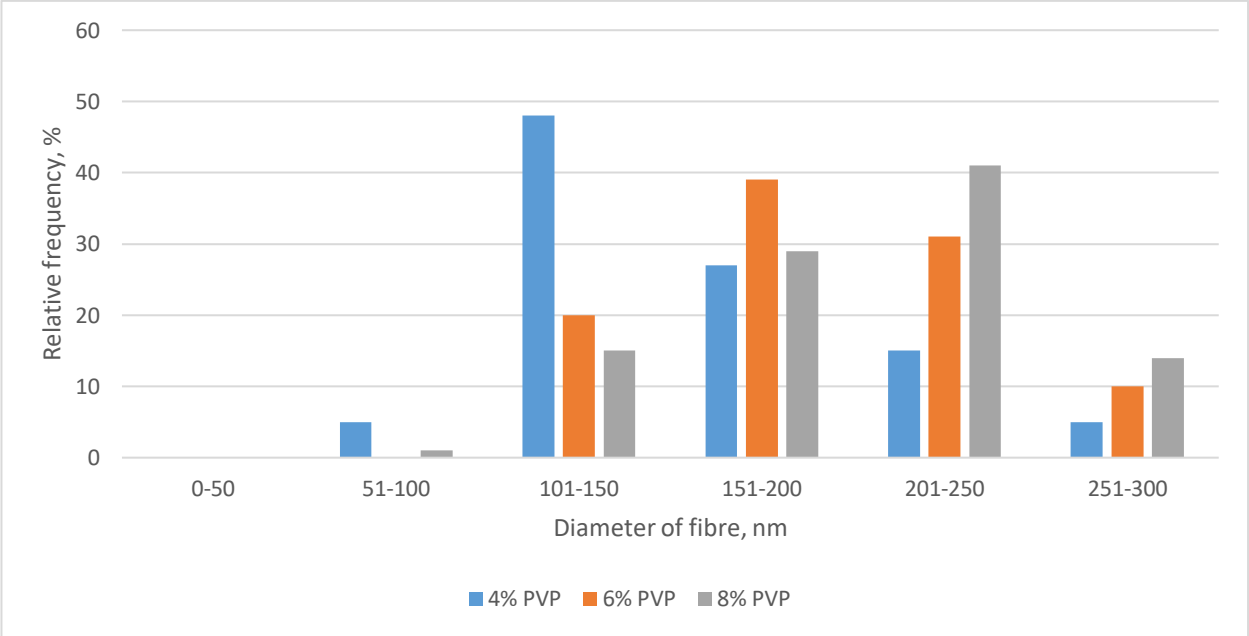


Figure 36. The diameter distribution of PVP nano/micro fibres from the ethanolic solutions of 4%, 6% and 8% PVP concentrations

Furthermore, it might be also noticed that the mean values of a fibre diameter (Table 9) rose with the increase of polymer concentration. The same tendency was performed in the research work of Nasouri et al. [67] in electrospinning with PVP polymer. It proved once again that with polymer concentration increase, viscosity increases, and the diameter of fibre becomes greater too. Finally, the standard deviation *SD* and the coefficient of variation *CV* values of nano/micro fibres might be considered as common ones when fibres are formed by electrospinning technology (*SD* fluctuated from 24 to 37 nm and *CV* changed from 15 to 19%).

Table 9. Mean values of fibre diameter and average porosity values

| **Composition of an electrospun solution** | **Mean value of fibre diameter $A_d \pm SD$, nm** | **Coefficient of variation *CV*, %** | **Average porosity $A_p \pm SE$, %** |
|---|---|---|---|
| 4% PVP + 96% $C_2H_6O$ | 162 ± 24 | 15 | 84 ± 1,2 |
| 6% PVP + 94% $C_2H_6O$ | 191 ± 36 | 19 | 87 ± 1,0 |
| 8% PVP + 92% $C_2H_6O$ | 206 ± 37 | 18 | 92 ± 2,0 |

Another indicator to discuss the structure of nonwoven fabric is porosity. It is especially important parameter for biomedical applications and filtration. As it can be seen in Table 9, the porosity of electrospun materials were $A_p$ = 84 ± 1,2% for the 4% PVP solution, and it sequentially increased with the polymer concentration increase. This might be explained by slower Tailor cones formation when polymer concentration is higher meaning thicker nano/micro fibres are formed with greater volume of voids. The standard deviations of the porosity measurement are small and consistent. Contrariwise, V. Elayappan et al. [68] obtained that $TiO_2$ nanofibres from 5% PVP solution had higher porosity than those obtained from 8% and 10% PVP solutions.

### 3.2. Formation of Nano/Micro Fibres from Ethanolic PVP Solutions with Different Ratios of Ag NPs

The second part of experimental work was continued with **ethanolic solutions only**, as the usage of water as a solvent was not successful.

Table 10. Surface tension, viscosity of pure PVP and PVP/Ag NPs electrospun solutions

| **Sample** | **Composition of an electrospun solution** | **Surface tension $\gamma \pm SE$, mN/m** | **Viscosity $\eta \pm SE$, mPa·s** | **Electrical conductivity $\sigma \pm SE$, µS/cm** |
|---|---|---|---|---|
| 1 | 4% PVP | 23,09 ± 0,27 | 104 ± 10 | 3,32 ± 0,11 |
| 2 | 4% PVP/0,001% Ag NPs | 23,10 ± 0,27 | 102 ± 10 | 4,21 ± 0,11 |
| 3 | 4% PVP/0,005% Ag NPs | 23,13 ± 0,30 | 103 ± 11 | 7,70 ± 0,12 |
| 4 | 4% PVP/0,02% Ag NPs | 23,22 ± 0,30 | 89 ± 12 | 5,27 ± 0,12 |
| 5 | 6% PVP | 22,54 ± 0,19 | 170 ± 13 | 2,80 ± 0,12 |
| 6 | 6% PVP/0,001% Ag NPs | 22,56 ±0,20 | 172 ± 11 | 3,37 ± 0,12 |
| 7 | 6% PVP/0,005% Ag NPs | 22,59 ± 0,19 | 168 ± 12 | 6,30 ± 0,13 |
| 8 | 6% PVP/0,02% Ag NPs | 22,78 ± 0,24 | 148 ± 11 | 4,93 ± 0,13 |
| 9 | 8% PVP | 21,64 ± 0,19 | 325 ± 14 | 3,42 ± 0,12 |
| 10 | 8% PVP/0,001% Ag NPs | 21,64 ± 0,17 | 321 ± 13 | 4,10 ± 0,14 |
| 11 | 8% PVP/0,005% Ag NPs | 21,65 ± 0,17 | 315 ± 13 | 5,90 ± 0,13 |
| 12 | 8% PVP/0,02% Ag NPs | 21,94 ± 0,14 | 299 ± 12 | 5,30 ± 0,14 |

It is well known that the structure of a nano/micro fibres material is highly affected by the properties of an electrospun solution. Therefore, the interest was to test solutions having the content of Ag NPs whether it impacts properties as the surface tension and the viscosity of a solution. The data obtained (Table 10) shows that the inclusion of 0,001% Ag NPs into the solution had no influence on surface tension in comparison with the pure PVP solutions. Although, the slight increase of surface tension

can be seen when the concentration of Ag NPs became 0,02%, for instance, the surface tension of the 8% PVP solution was $\gamma$ = 21,64 ± 0,19 mN/m while the one of 8% PVP/0,02% Ag NPs was $\gamma$ = 21,94 ± 0,14 mN/m.

In addition, the measurement of viscosity decreased indistinctly with the increase of the concentration of Ag NPs. However, the substantial difference was obtained between the pure PVP solutions and the ones with 0,02% Ag NPs. For example, the viscosity of the 6% PVP solution was $\eta$ = 170 ± 13 mPa·s and the viscosity of the 6% PVP/0,02% Ag NPs solution was $\eta$ = 148 ± 11 mPa·s. To sum up, the concentration of Ag NPs had a slight influence on solution parameters.

Moreover, the electrical conductivity readings of solutions are exhibited in Table 10. The values of the electrical conductivity of pure PVP solutions were obtained the lowest and no tendency was observed between them. However, with the addition of Ag NPs an increase was achieved with all different PVP concentrations. Clear depiction is given in Figure 37. The electrical conductivity of solutions having 0,005% Ag NPs demonstrated the highest conductivity. Nevertheless, the reduction of the electrical conductivity of solutions with the 0,02% Ag NPs content is observed. Due to the low dielectric permittivity in ethanolic solutions, not only dissociation of molecules but also association occurred, thus more ionic pairs were generated. When the concentration of silver ions in a solution was increasing and finally equilibrium line was exceeded, ions conjugated into neutral ionic pairs, hence the electrical conductivity was decreased. [69]

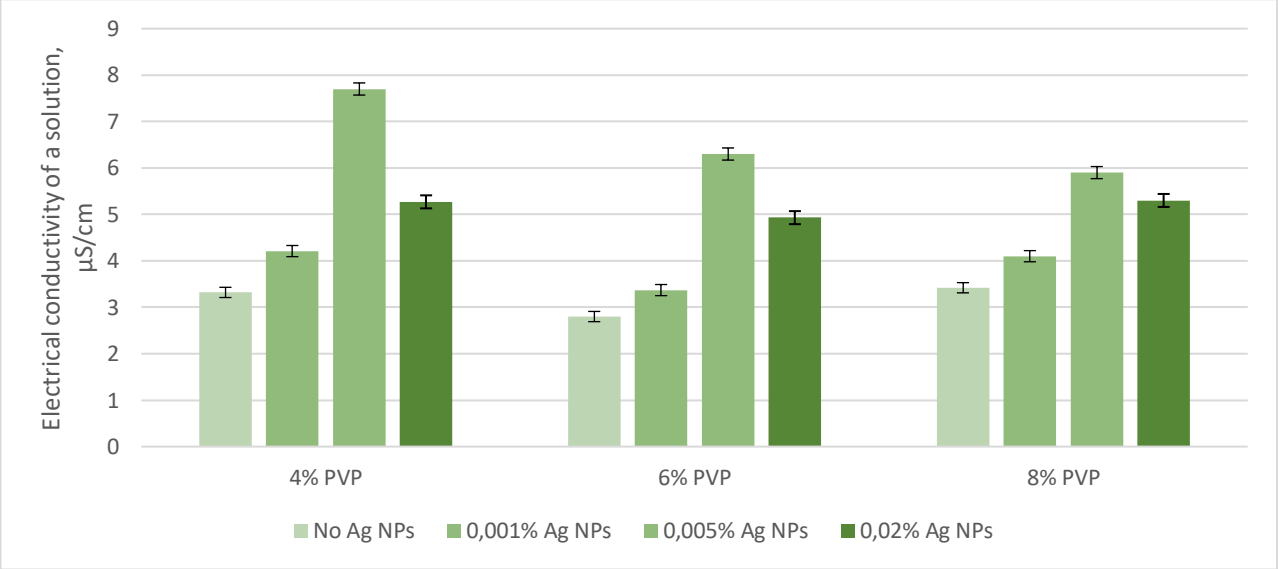


Figure 37. The electrical conductivity of PVP solutions with different concentrations of Ag NPs

The same results were received in other scientific works wherein it was indicated that the increased amount of Ag NPs increased the conductivity of a polymer solution, thus it led to increased columbic forces. This phenomenon resulted in polymer jet splitting and formation of thinner fibres with less defects formed. [44, 70]

The significant indicator of the conductivity of solutions could be electric current given by electrospinning equipment "Nanospider$^{TM}$" (see Table 11). Electric current was increasing with an increased polymer concentration in a solution. For instance, during electrospinning process with 4% PVP solution the electric current $I$ = [0,005, 0,007] mA was detected, and it decreased when 0,001% Ag NPs was presented in the solution, the electric current was $I$ = [0,012, 0,014] mA. According to

the calculations, the mean values of fibre diameter decreased with the increase of electric current flow due to Ag NPs presence in solutions. For example, the mean value of 6% PVP nano/micro fibres diameter was $A_d$ = 191 ± 36 nm (*CV* = 19%) while the mean value of 6% PVP/0,001% Ag NPs fibres diameter was $A_d$ = 161 ± 27 nm (*CV* = 17%), therefore electric current was *I* = [0,007, 0,009] mA and *I* = [0,010, 0,012] mA, respectively. The same tendency was observed with 8% PVP electrospun solutions.

Table 11. Electric current variations and mean values of fibres diameter

| Sample | Composition of an electrospun solution | Electric current *I*, mA | The mean value of fibre diameter $A_d \pm SD$, nm | Coefficient of variation *CV*, % |
|---|---|---|---|---|
| 1 | 4% PVP | [0,005, 0,007] | 162 ± 24 | 15 |
| 2 | 4% PVP/0,001% Ag NPs | [0,012, 0,014] | 137 ± 25 | 18 |
| 3 | 4% PVP/0,005% Ag NPs | [0,014, 0,018] | 133 ± 28 | 21 |
| 4 | 4% PVP/0,02% Ag NPs | [0,014, 0,020] | 102 ± 21 | 21 |
| 5 | 6% PVP | [0,005, 0,009] | 191 ± 36 | 19 |
| 6 | 6% PVP/0,001% Ag NPs | [0,010, 0,012] | 161 ± 27 | 17 |
| 7 | 6% PVP/0,005% Ag NPs | [0,012, 0,016] | 139 ± 24 | 17 |
| 8 | 6% PVP/0,02% Ag NPs | [0,015, 0,020] | 110 ± 22 | 20 |
| 9 | 8% PVP | [0,007, 0,010] | 206 ± 37 | 18 |
| 10 | 8% PVP/0,001% Ag NPs | [0,008, 0,014] | 164 ± 31 | 19 |
| 11 | 8% PVP/0,005% Ag NPs | [0,016, 0,018] | 142 ± 27 | 19 |
| 12 | 8% PVP/0,02% Ag NPs | [0,016, 0,022] | 113 ± 25 | 22 |

**The morphology of the nano/micro fibres from 8% PVP solutions with different Ag NPs ratios**

It is evident when taking a look at Figure 38, visibly the diameter of nano/micro fibres increased with the increase of Ag NPs concentration. For instance, the nano/micro fibres from the pure 8% PVP solution (Fig. 38 (a)) are clearly thicker than the ones from the 8% PVP/0,005% Ag NPs solution (Fig. 38 (c)). Nevertheless, only a small difference can be considered when comparing the 8% PVP electrospun material (Fig. 38 (a)) with the 8% PVP/0,001% Ag NPs one (Fig. 38 (b)). Finally, the finest nano/micro fibres were observed in Fig. 38 (d) due to the highest concentration of Ag NPs (0,02%). In all the photographs of 8% PVP materials, electrospun fibres are continuous and smooth. Nonetheless, the defect of a few merged fibres together remained in the structure even though Ag NPs were presented (see Fig. 38 (1)).

Furthermore, the diameter distribution diagram of 8% PVP electrospun fibres materials are indicated in Figure 39. The diameter of fibres were up to 150 nm in 16% cases from pure PVP solution, however the high frequency (42% of cases up to 150 nm) was obtained when 0,001% Ag NPs were added. Afterwards lower frequency was achieved, 54% and 58% of cases up to 150 nm were presented at 8% PVP/0,005% Ag NPs and 8% PVP/0,02% Ag NPs, respectively. Interestingly, the pure PVP nano/micro fibres diameters were over 150 nm in 84% of total cases while with 0,02% Ag NPs addition the diameter over 150 nm decreased to 42%. Hence, the viscosity did not significantly change with the increased amount of Ag NPs, however thinner nano/micro fibres were formed due to increased electrical conductivity of the solution. Even the small amount of Ag NPs strongly influenced the morphology of 8% PVP electrospun material.

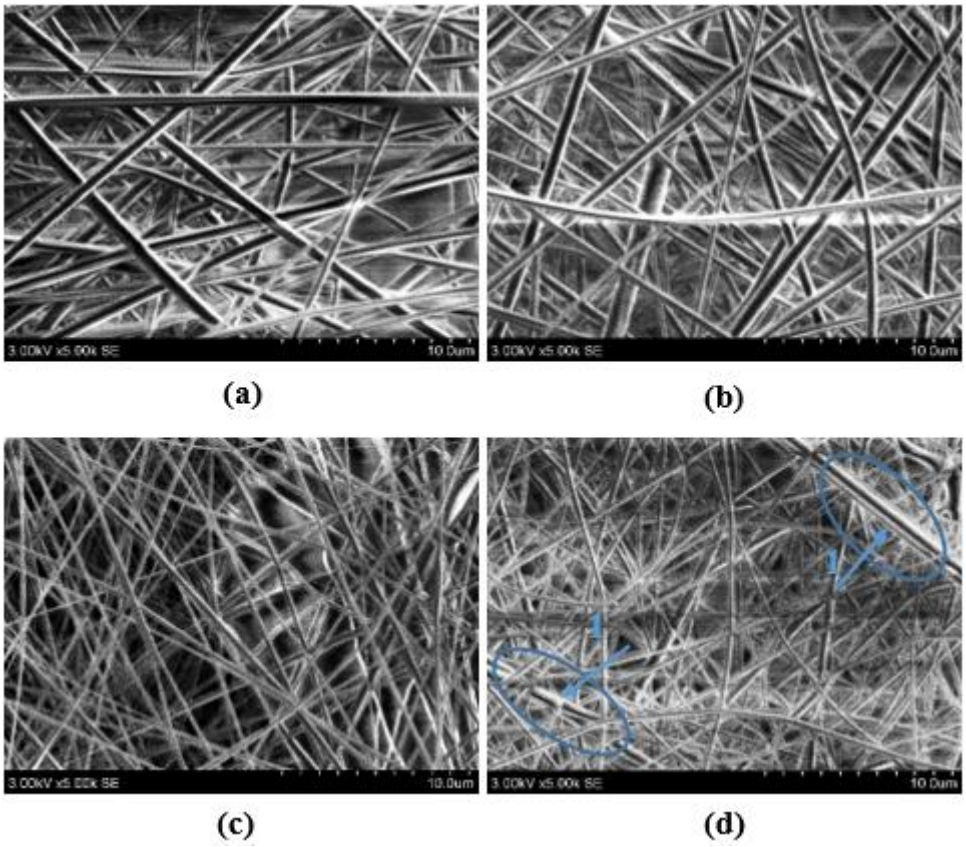


Figure 38. SEM images of nano/micro fibres from (a) 8% PVP, (b) 8% PVP/0,001% Ag NPs, (c) 8% PVP/ 0,005% Ag NPs and (d) 8% PVP/0,02% Ag NPs electrospun solutions (magnification ×5000, scale 10 $\mu$m); 1 – a bundle of stuck fibres

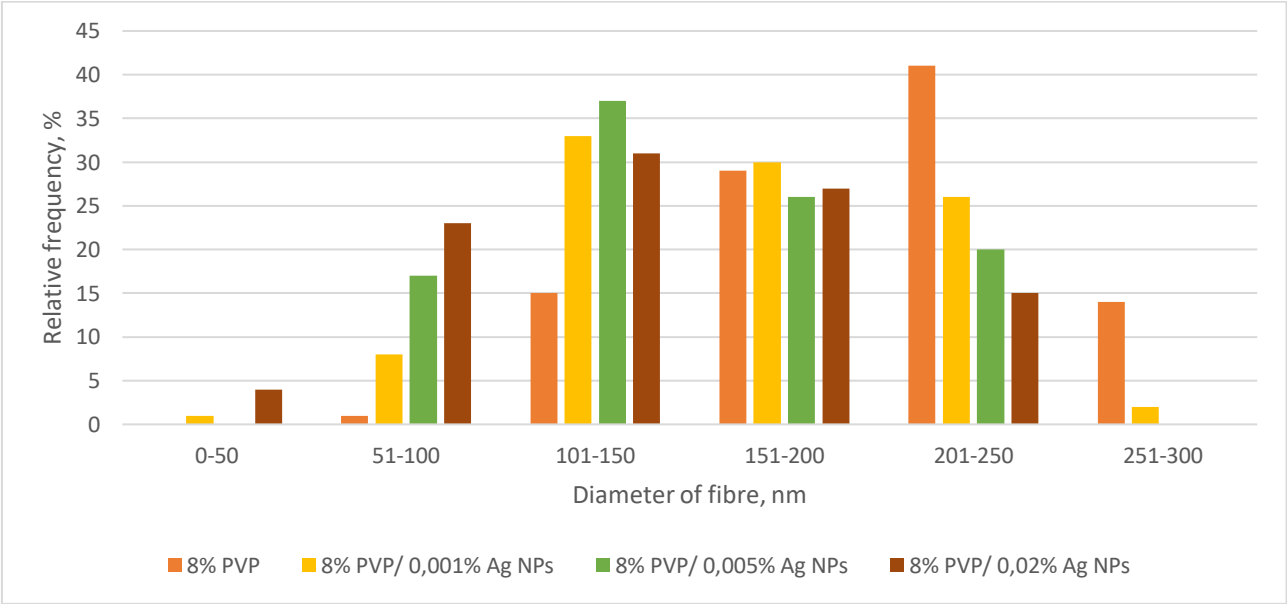


Figure 39. The diameter distribution of nano/micro fibres from solutions of 8% PVP concentration with different Ag NPs ratios

**The morphology of the nano/micro fibres from 6% PVP solutions with different Ag NPs ratios**

For the following results, electrospinning from 6% PVP with different Ag NPs ratios is reported. SEM images are demonstrated in Figure 40. The photographs showed quite smooth and uniform

morphology of nano/micro fibres without noteworthy defects. When looking attentively at SEM images, a gradual decrease in terms of fibre diameter might be observed with the increase of Ag NPs concentration, starting from Fig. 40 (a) and ending with Fig. 40 (d). This is related with increasing electrical conductivity when Ag NPs content is small (up to 0,005%) and especially decreased viscosity of the solutions including 0,02% Ag NPs amount. [44]

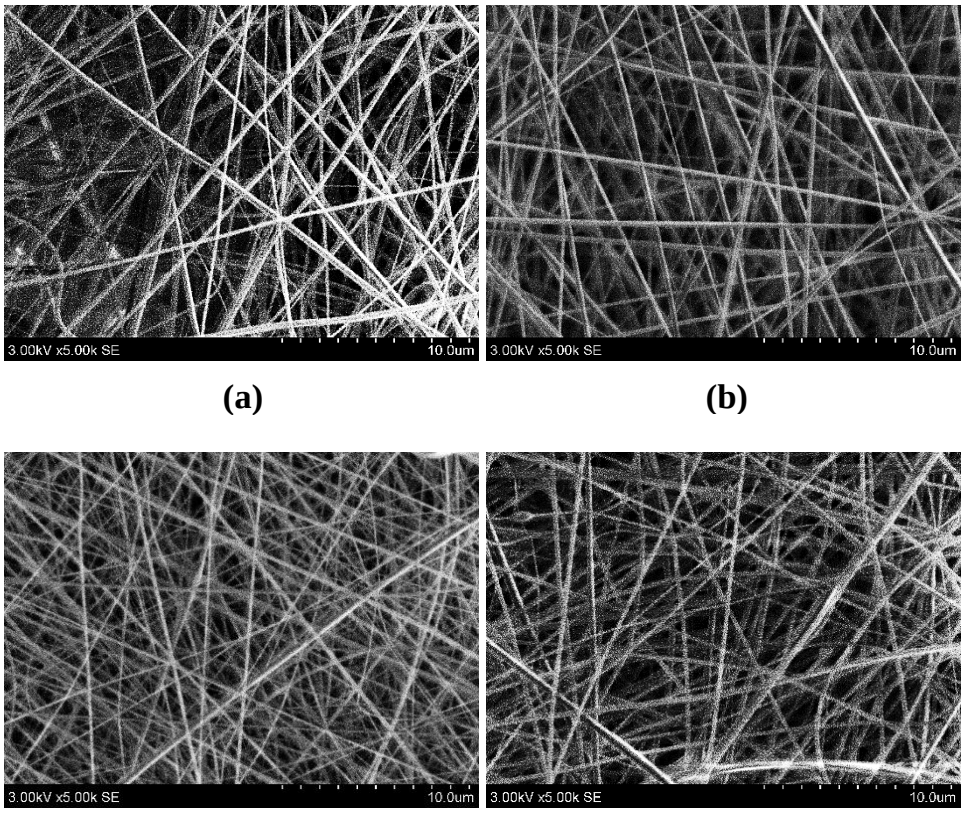


Figure 40. SEM images of nano/micro fibres from (a) 6% PVP, (b) 6% PVP/0,001% Ag NPs, (c) 6% PVP/ 0,005% Ag NPs and (d) 6% PVP/0,02% Ag NPs electrospun solutions (magnification ×5000, scale 10 $\mu$m)

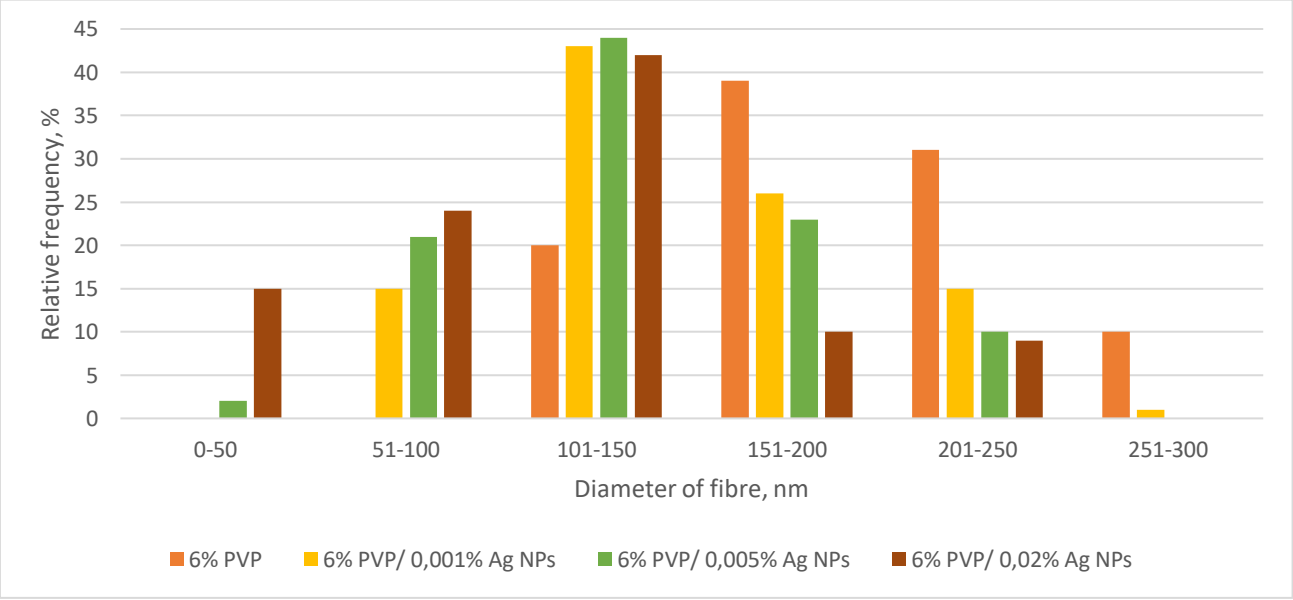


Figure 41. The diameter distribution of nano/micro fibres from solutions of 6% PVP concentration with different Ag NPs ratios

The diagram (Figure 41) demonstrates the distribution of nano/micro fibres from 6% PVP solutions with the different amount of Ag NPs. Clearly, the diameter of the fibres formed from pure 6% PVP solution was mostly in the range [151, 250] nm while the peaks of three other cases (6% PVP/0,001% Ag NPs, 6% PVP/0,005% Ag NPs and 6% PVP/0,02% Ag NPs) were in the range [101, 150] nm. Furthermore, the diameter of 6% PVP/0,02% Ag NPs nano/micro fibres were up to 150 nm in 81% of cases when the diameter of pure 6% PVP fibres were up to 150 nm in only 20% of cases. In addition, the frequency of the diameters of 6% PVP/0,005% Ag NPs and 6% PVP/0,001% Ag NPs nano/micro fibres up to 150 nm decreased gradually, 67% and 58%, respectively.

**The morphology of the nano/micro fibres from 4% PVP solutions with different Ag NPs ratios**

Lastly, the morphology of the nano/micro fibres from 4% PVP solutions with different amount of Ag NPs were investigated. SEM images are demonstrated in Figure 42. As it was discovered before, pure 4% PVP material had beads in the structure, however it was expected to be eliminated with the inclusion of Ag NPs due to increased conductivity, slightly decreased viscosity and jet splitting. Regrettably, a couple of beads were detected in 4% PVP/0,005% Ag NPs nano/micro fibres (Fig. 42 (1)). Although the cases of 4% PVP/0,001% Ag NPs (Fig. 42 (b)) and 4% PVP/0,02% Ag NPs (Fig. 42 (d)) had no visible defects from SEM photographs.

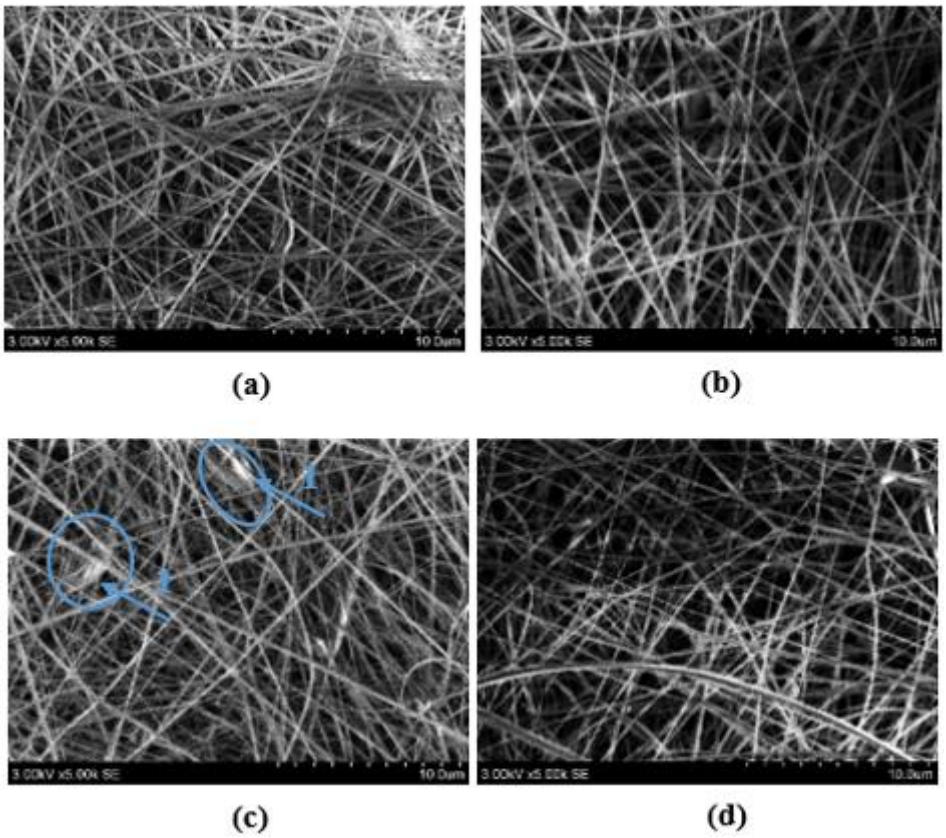


Figure 42. SEM images of nano/micro fibres from (a) 4% PVP, (b) 4% PVP/0,001% Ag NPs, (c) 4% PVP/ 0,005% Ag NPs and (d) 4% PVP/0,02% Ag NPs electrospun solutions (magnification ×5000, scale 10 $\mu$m); 1 – a bead

To consider nano/micro fibre thickness, the distribution diagram of fibre diameter was achieved (see Fig. 43). With the increasing Ag NPs content, the viscosity of solutions decreased indistinctly, meanwhile the increase of the conductivity was evident, thus thinner nano/micro fibres were formed.

For example, when pure 4% PVP solution was electrospun, the fibre diameter up to 150 nm was in 53% cases. When 0,001% Ag NPs into a solution were introduced, the frequency of the fibre diameter up to 150 nm increased to 59%. Moreover, the frequency of the diameters of 4% PVP/0,005% Ag NPs and 4% PVP/0,02% Ag NPs nano/micro fibres up to 150 nm became greater, 72% and 83%, respectively.

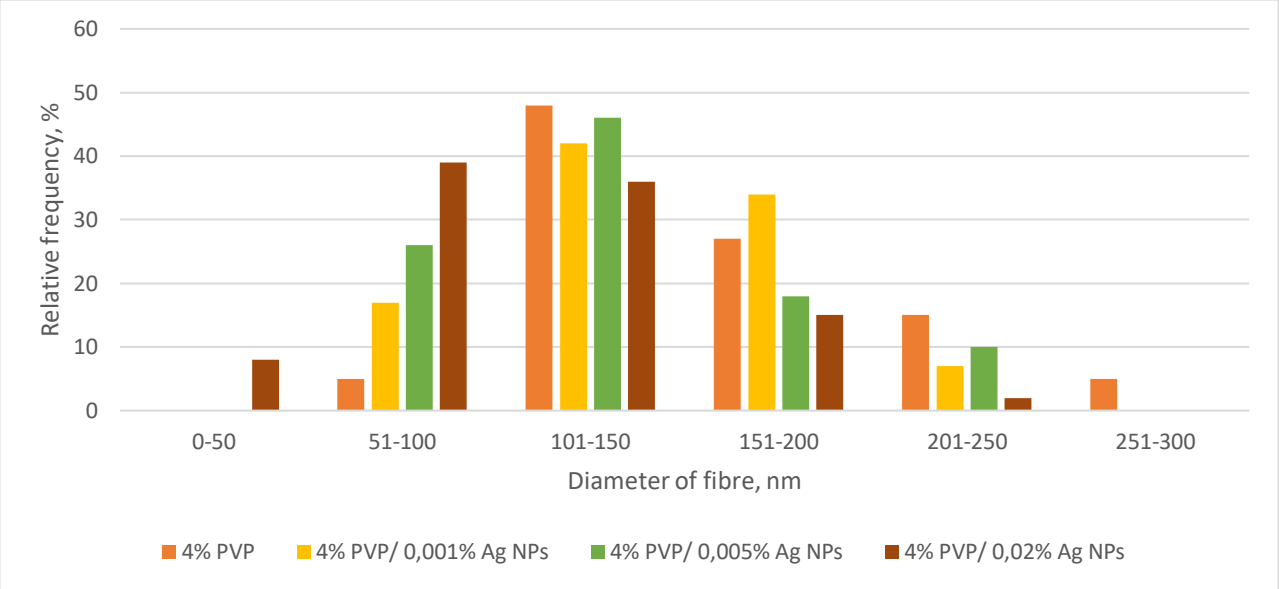


Figure 43. The diameter distribution of nano/micro fibres from solutions of 4% PVP concentration with different Ag NPs ratios

**Comparison of the morphology of fibres from solutions with different amount of PVP and Ag NPs**

From the histograms presented in Fig. 39, Fig. 41 and Fig. 43 it can be asserted that even the small amount of Ag NPs induced the formation of thinner PVP fibres. The addition of 0,001% and 0,005% Ag NPs into PVP solutions increased the frequency of fibres with a diameter up to 150 nm up to 2,5 and 3 times, respectively. Fibres with the smallest diameters where electrospun from the solutions with the lowest PVP and the highest Ag NPs concentrations. From 4% PVP/0,02% Ag NPs solution, 84% of fibres with the diameter up to 150 nm were measured. Moreover, from this solution 47% of the fibres with the diameter up to 100 nm were recorded, thus those fibres might be stated as nanofibers. The formation of the thinner fibres from the solutions with 0,02% Ag NPs is caused more by decreased viscosity then the electric conductivity of PVP solutions. Hence, not only the concentration of a polymer had an influence on ultra-fine fibres formation but the amount of Ag NPs as well.

**The porosity of electrospun PVP materials with different Ag NPs ratios**

It is well known that the highly porous materials allows the transit of gas. A high porosity material has a good gas breathability and a water-tightness ability. Hence, this kind of materials has a potential application in wound healing or postoperative anti-adhesion areas. Unfortunately, no research works considering the porosity of electrospun PVP materials were found. [71]

The calculated average values of porosity are shown in Table 12. As characterised in the previous subsection, the average porosity increased with increasing PVP concentration. When the very small

amount of Ag NPs were added into a solution, no significant changes were observed with cases of 4% and 6% PVP. For example, pure 6% PVP had the average porosity $A_p$ = 87% (*SE* = 1,0 %) and 6% PVP with 0,005% Ag NPs had the average porosity $A_p$ = 86% (*SE* = 1,5%). In spite of that, an increase can be noticed when comparing pure 4% PVP nano/micro fibres materials with 4% PVP/ 0,02% Ag NPs nano/micro fibres materials, the average porosity was $A_p$ = 84% (*SE* = 1,2 %) and $A_p$ = 79% (*SE* = 2,0 %), respectively.

Table 12. The average porosity values of nano/micro fibres materials

| Sample | Composition of an electrospun solution | Average porosity $A_p \pm SE$, % |
|---|---|---|
| 1 | 4% PVP | 84 ± 1,2 |
| 2 | 4% PVP/0,001% Ag NPs | 83 ± 1,5 |
| 3 | 4% PVP/0,005% Ag NPs | 83 ± 1,5 |
| 4 | 4% PVP/0,02% Ag NPs | 79 ± 2,0 |
| 5 | 6% PVP | 87 ± 1,0 |
| 6 | 6% PVP/0,001% Ag NPs | 87 ± 0,6 |
| 7 | 6% PVP/0,005% Ag NPs | 86 ± 1,3 |
| 8 | 6% PVP/0,02% Ag NPs | 84 ± 1,8 |
| 9 | 8% PVP | 92 ± 2,0 |
| 10 | 8% PVP/0,001% Ag NPs | 88 ± 1,9 |
| 11 | 8% PVP/0,005% Ag NPs | 87 ± 1,0 |
| 12 | 8% PVP/0,02% Ag NPs | 84 ± 0,6 |

Furthermore, the highest value of the average porosity was received in the case of 8% PVP nano/micro fibres material. When comparing it with the material having the highest 0,02% Ag NPs content, 8% of decrease is presented. The average porosity of 8% PVP material was $A_p$ = 92% (*SE* = 2,0%) and the average porosity of 8% PVP with 0,02% Ag NPs material was $A_p$ = 84% (*SE* = 0,6%).

Finally, it could be stated the inclusion of Ag NPs had an influence on the porosity of nano/micro fibres material. The average porosity decreased with all the cases, in regard to the same polymer concentration when Ag NPs were added. And besides, with the same amount of Ag NPs but different PVP concentration, the porosity remained greater with higher polymer concentration. For instance, the average porosity of 4% PVP/0,001% Ag NPs electrospun material was $A_p$ = 83% (*SE* = 1,5%) while average porosity of 6% PVP/0,001% Ag NPs electrospun material was $A_p$ = 87% (*SE* = 0,6%).

**Detection of Silver Nanoparticles in electrospun PVP materials**

Elemental analysis of electrospun PVP materials containing Ag NPs was performed by SEM-EDS. The aim was to detect silver whether it remains in produced electrospun materials. EDS analysis exhibited a silver content when the highest Ag NPs content (0,02%) was presented with 4%, 6% and 8% PVP. Spectra of 4% PVP/0,02% Ag NPs, 6% PVP/0,02% Ag NPs and 8% PVP/0,02% Ag NPs are depicted in Fig. 44, Fig. 45 and Fig. 46, respectively. Electrospun PVP materials having extremely small amount of Ag NPs (0,001% and 0,005%) was not detected due to their distribution mostly in a fibre matrix rather than on the surface of a fibre.

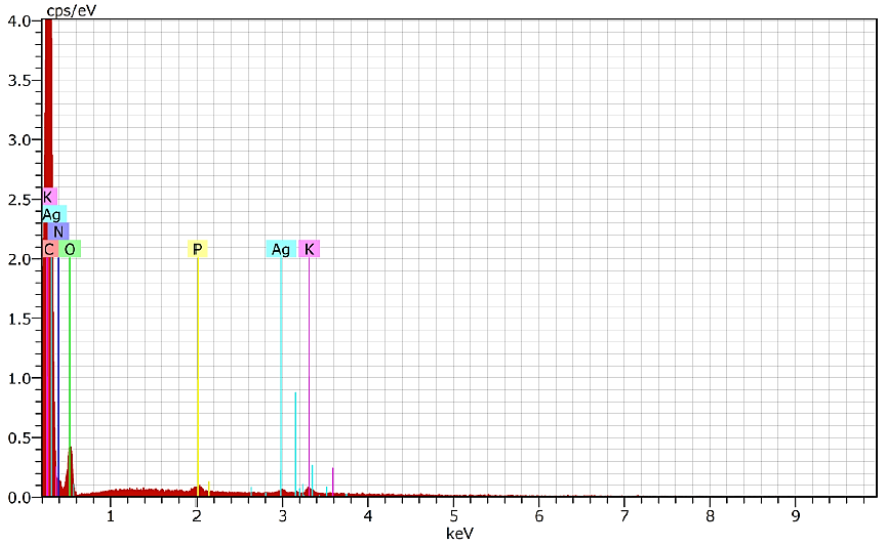


Figure 44. EDS spectra of the nano/micro fibres material from the 4% PVP/0,02% Ag NPs solution

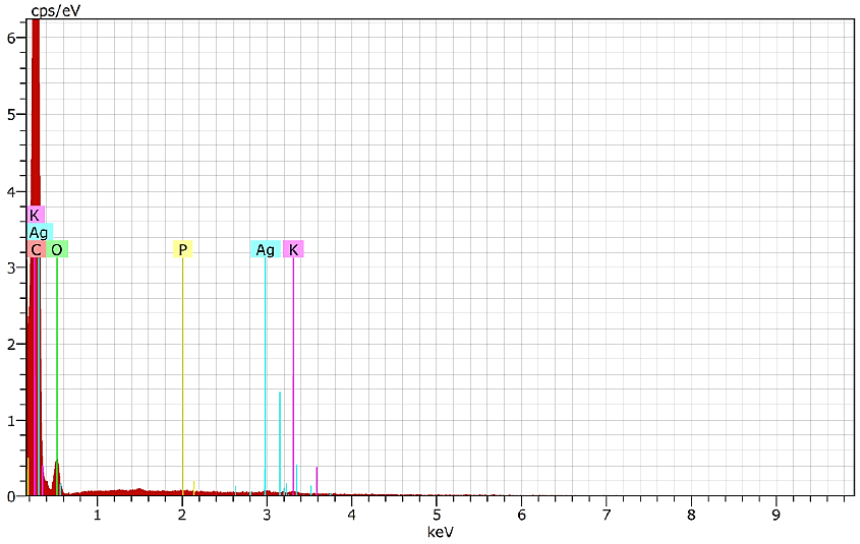


Figure 45. EDS spectra of the nano/micro fibres material from the 6% PVP/0,02% Ag NPs solution

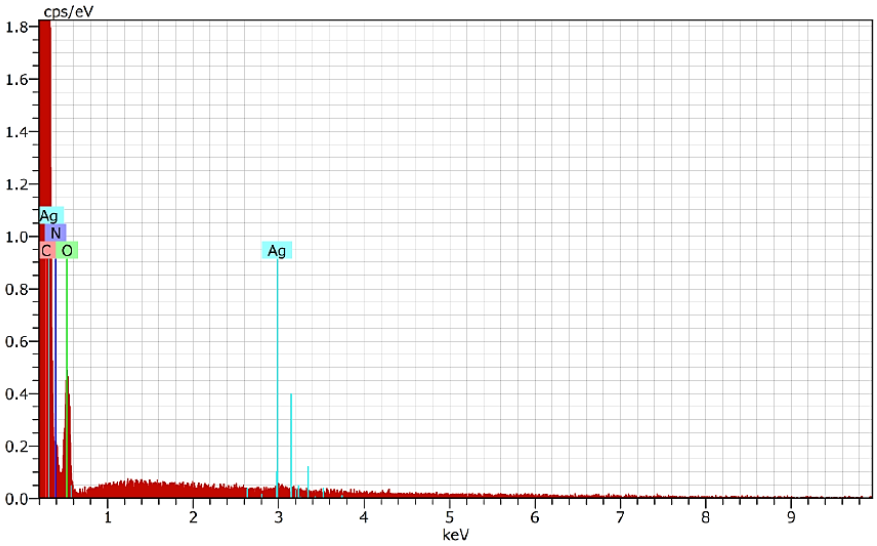


Figure 46. EDS spectra of the nano/micro fibres material from the 8% PVP/0,02% Ag NPs solution

### 3.3. Analysis of Antibacterial Activity of Nano/Micro Fibres Materials

Kirby-Bauer test (disk-diffusion method) was performed in order to test antibacterial activity of produced nano/micro fibres materials. Two microorganisms' colonies, named Gram-negative *E. coli* and Gram-positive *S. aureus*, were applied on 9 samples containing different ratios of Ag NPs and a reference (without Ag NPs). The photographs of inhibition zones of PVP/Ag NPs nano/micro fibres against *S. aureus* are demonstrated in Figure 47 and against *E. coli* in Figure 48.

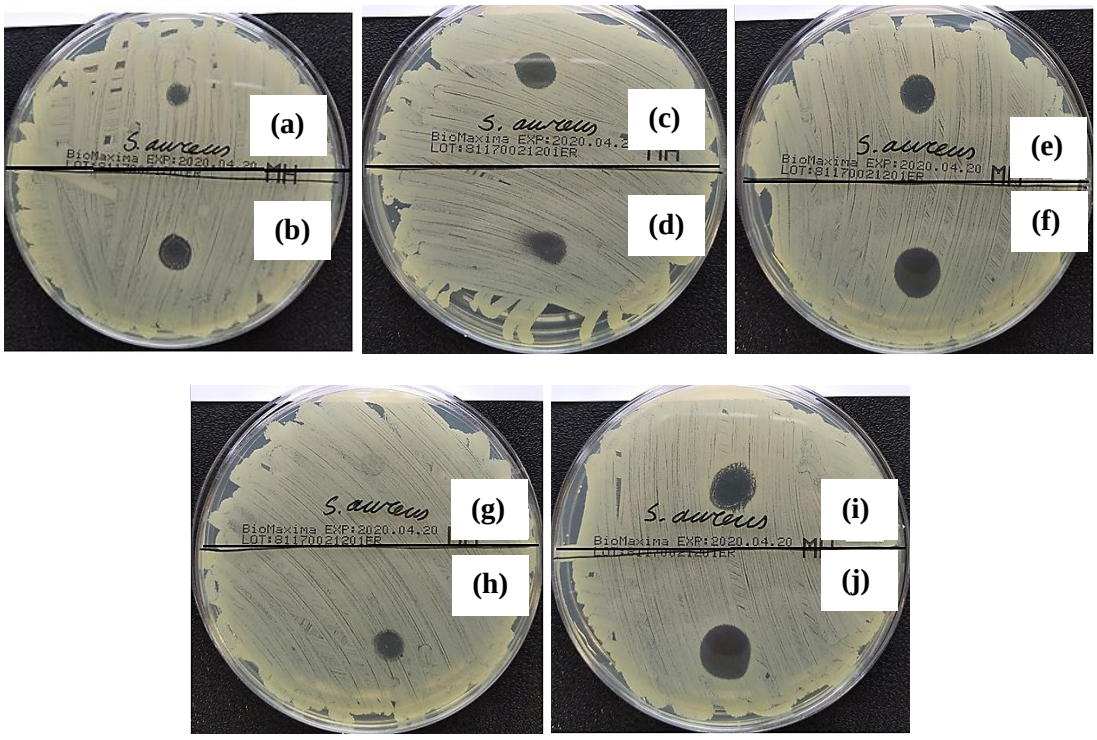


Figure 47. Test results of antibacterial activity against *S. aureus*; incubated with electrospun materials containing (a) 4% PVP/0,001% Ag NPs, (b) 4% PVP/0,005% Ag NPs, (c) 4% PVP/ 0,02%Ag NPs, (d) 6% PVP/0,001% Ag NPs, (e) 6% PVP/0,005% Ag NPs, (f) 6% PVP/0,02% Ag NPs, (g) 8% PVP, (h) 8% PVP/0,001% Ag NPs, (i) 8% PVP/0,005% Ag NPs, (j) 8% PVP/0,02% Ag NPs

Results showed that the inhibition zones measurements exhibited consistent inhibition with the increase of Ag NPs inclusion (see Table 13.). It can be confirmed that even the very small amount of Ag NPs content exhibited antibacterial property. However, the electrospun 4% PVP materials with all ratios of Ag NPs did not demonstrated a significant antibacterial activity. In all the cases, the content of 0,001% Ag NPs performed the partial inhibition of microorganisms' growth while 0,005% Ag NPs content indicated complete inhibition zone against both bacteria.

It should be emphasised that the highest activity was recorded in the samples of 8% PVP solution with 0,005% Ag NPs (11 mm inhibition zone for both microorganisms) and 0,02% Ag NPs (13 mm inhibition zone against *S. aureus* and 14 mm against *E. coli*). It might be explained by thicker nano/micro fibres formation from the solutions of higher polymer concentration meaning greater amount of Ag NPs had a possibility to spread and be fixed in a nano/micro fibre matrix. In addition, the electrospun 6% PVP/0,02% Ag NPs material showed the relatively high inhibition of both Gram-negative and Gram-positive microorganisms. It might be stated that even the small quantity of Ag NPs can exhibit comparatively high antibacterial impact. The same results were obtained by E.

Adomavičiūtė et al [29]. Inclusion of Ag NPs into electrospun solutions of PVP/PEE (propolis ethanolic extract) increased the antimicrobial activity.

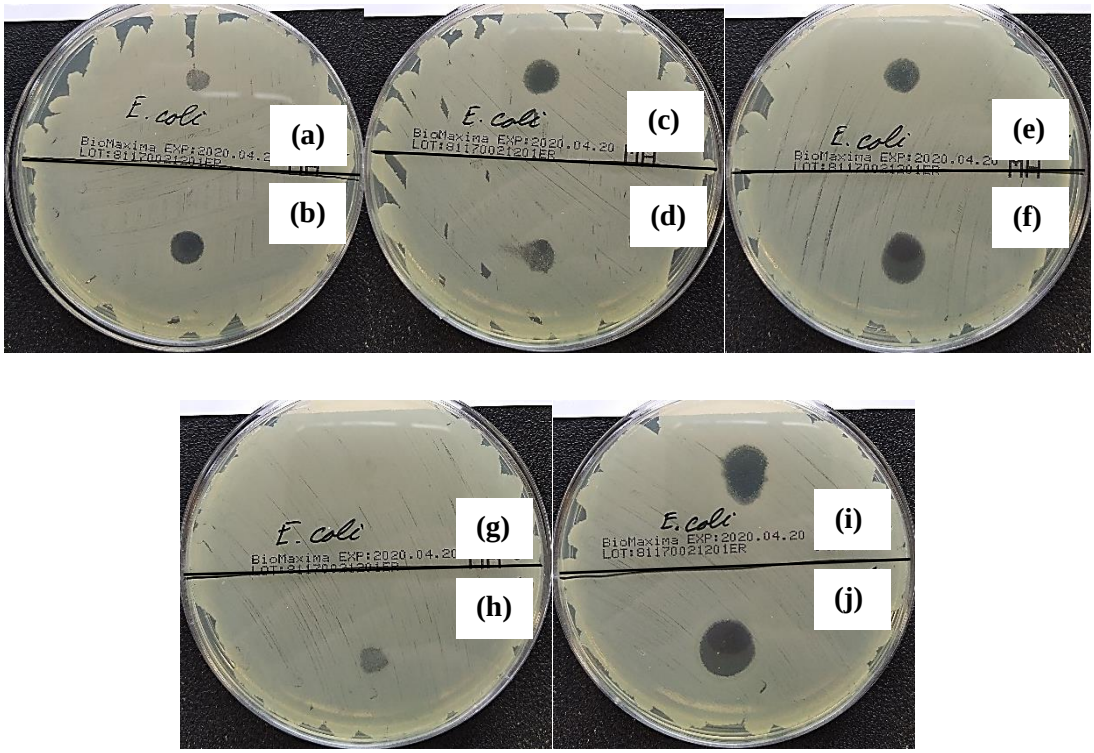


Figure 48. Test results of antibacterial activity against *E. coli*; incubated with electrospun materials containing (a) 4% PVP/0,001% Ag NPs, (b) 4% PVP/0,005% Ag NPs, (c) 4% PVP/0,02% Ag NPs, (d) 6% PVP/0,001% Ag NPs, (e) 6% PVP/0,005% Ag NPs, (f) 6% PVP/0,02% Ag NPs, (g) 8% PVP, (h) 8% PVP/ 0,001% Ag NPs, (i) 8% PVP/0,005% Ag NPs, (j) 8% PVP/0,02% Ag NPs

Table 13. Inhibition zones against *S. aureus* and *E. coli*

| **Composition of an electrospun solution** | **Inhibition zone against *S. aureus*, mm** | **Inhibition zone against *E. coli*, mm** |
|---|---|---|
| 4% PVP/0,001% Ag NPs | 6* | 6* |
| 4% PVP/0,005% Ag NPs | 9 | 8 |
| 4% PVP/0,02% Ag NPs | **10** | 9 |
| 6% PVP/0,001% Ag NPs | 7 | 8* |
| 6% PVP/0,005% Ag NPs | 9 | 9 |
| 6% PVP/0,02% Ag NPs | **12** | **11** |
| 8% PVP | 0 | 0 |
| 8% PVP/0,001% Ag NPs | 8 | 7* |
| 8% PVP/0,005% Ag NPs | **11** | **11** |
| 8% PVP/0,02% Ag NPs | **13** | **14** |

*partially inhibited the growth of bacteria, discrete small colonies are seen

## 4. Conclusions

1. It was not possible to produce nano/micro fibres from 4%, 6% and 8% PVP aqueous solutions by means of the needleless roller electrospinning equipment. Under the same spinning conditions nano/micro fibres were successfully formed from pure PVP and PVP with different contents of Ag NPs, that are produced by a new patented technology, ethanolic solutions.

2. The concentration of PVP polymer had an influence on the viscosity of solutions which increased 3 times when the concentration of PVP polymer in the solution increased from 4% to 8%. The surface tension and the conductivity of polymer solutions did not change significantly with increased polymer concentration.

3. It was identified that the insertion of the very small amount (up to 0,005%) of Ag NPs into a PVP solution did not affect the viscosity and the surface tension of electrospun solutions but caused the increase of the electrical conductivity of solutions to 2 times. The addition of the greater amount (0,02%) of Ag NPs caused the decrease of the electrical conductivity of solutions.

4. The PVP polymer concentration in ethanolic solutions had the substantial influence on the morphology and the structure of the materials formed by means of the needleless roller electrospinning system. Electrospun materials with the thickest nano/micro fibres (mean value of fibre diameter was 206 nm) and the highest average porosity (92%) were spun from 8% PVP solution. Herewith, the materials formed from 4% PVP solution had nano/micro fibres with the mean value of fibre diameter 162 nm and the average porosity 84%.

5. Nano/micro fibres from ethanolic 4% PVP and 8% PVP solutions were obtained with a couple of defects. A few beads (in 4% PVP electrospun materials) and bundles of fibres that are stuck together (in 8% PVP electrospun materials) were detected in the structures. Beaded-free nano/micro fibres from 6% PVP solutions were obtained.

6. It was found that Ag NPs had the influence on the morphology of electrospun PVP materials. The addition of Ag NPs into a solution allowed to form more nano/micro fibres with a diameter up to 150 nm in comparison with the pure PVP solutions. Thinner fibres and denser materials were formed with higher concentration of Ag NPs. In the materials formed from 4% PVP/0,02% Ag NPs solution, 47% of the nanofibers with the diameter up to 100 nm were recorded. This material exhibited the lowest value of the porosity (79%).

7. The antibacterial activity results exhibited a comparatively high influence of the small amount of Ag NPs against Gram-negative and Gram-positive colonies. The highest concentration of Ag NPs in PVP materials demonstrated the highest antibacterial effect. Even electrospun materials with thick nano/micro fibres and the 0,005% Ag NPs content demonstrated the inhibition zone higher than 10 mm against both types of microorganisms.

## 5. Recommendations

Regarding to the obtain results and additional expectations, the further studies of PVP materials, formed by means of the needleless roller electrospinning system, might be recommended:

1. Usage of water as a green solvent should be improved by mixing it with additives that exhibits lower surface tension in terms of reducing the overall surface tension of an electrospun solution.

2. Evaluation of cytotoxicity of electrospun materials from PVP solutions with different Ag NPs contents might be accomplished.

3. Formation of PVP electrospun materials could be formed with Ag NPs that are produced by different methods, thus comparison could be performed in regards of testing antibacterial activity and cytotoxicity as well.

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