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# Influence of inorganic additives on morphology of electrospun fibres

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**ABSTRACT**

**Purpose:** This paper describes the effect of inorganic additives and operating parameters of an electrospinning process on electrospun fiber diameters and morphology.

**Design/methodology/approach:** Application of different solvents and process parameters impact characteristics of the micro and nanofibers made of PEO and also PVA with CuOAc.

**Findings:** The results show that the three parameters (volumetric charge density, distance from nozzle to collector, and viscosity) have the most significant effect on the electrospun fiber morphology. The nano- and microfibers produced were characterized by scanning electron microscopy as well as with use of image analyzing tool DigitalMicrograph. Changes in length of stream and volatility of the solvent influence the shape of the fibres and internal solution load. The resulting fibre shape shows that for shorter distances the process was unstable, and the morphology of the filaments from a longer distance shows the gradual stabilization and indicates optimal process parameters.

**Practical implications:** Based on the research carried out it is clear that micro and nanofiber characteristics vary widely depending on prepared solutions and process parameters.

**Originality/value:** It was confirmed that inorganic additives, solvent type and process parameters have an effect on morphological aspects of produced micro and nanofibres.

**Keywords:** Fibre electrospinning; Polyethylene oxide; Microfibers; Nanofibers; Nanocomposites

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**METHODOLOGY OF RESEARCH**

## 1. Introduction

Nanofibres are one-dimensional nanostructures in form of fibres from various materials. They are characterised by being considerably longer than their cross sectional diameter. Polymer nanofibres can be made by variety of methods. The most common techniques are: electrospinning, using template synthesis, phase separation, molecular self-assembly, and drawing. There are several types of nanofibers [1-6]:

- nanofibres with beads: fibres resulting from low viscosity solutions, during increasing viscosity beads changing its shape from spherical to more spindly,

- porous nanofibres: obtained in a high humidity environment, pore size can be modified by process parameters and solution components,
- flat nano-ribbons: formation these fibres is directly related to the rate of solvent evaporation. When the fibres collect on the collector they are still wet in the shape of flat ribbons,
- hollow nanofibres - production consists of three stages; electrospinning, chemical vapour deposition coating on electrospun fibres and removal of the core material. Hollow nanofibres can also be obtained by spinning in a coaxial orientation, this method consists of a one stage process,
- branched nanofibres- produced by altering equilibrium parameters of electrical and surface tension forces.
- nanofibres with core structures- possible to obtain from polymer solution containing two polymers. Polymer phase is separated while solvent is evaporated.

## 2. Target and scope of the researches

The main target of the undertaken research was to investigate the influence of inorganic additives and electrospinning process parameters on morphology and fibre diameter for two types of polymers: polyethylene oxide (PEO) and polyvinyl alcohol (PVA). Both polymers were prepared with different types of solvents and concentrations before electrospinning. Polyethylene oxide is a hygroscopic white powder, is non-toxic and dissolves in many solvents. It is used primarily as a viscosity modifier in medicine, pharmacy and cosmetology [9]. Because of it's biocompatibility and water solubility it can be used as carrier for drugs in the body or in a biocompatible hydrogel [8-10]. PVA is nontoxic polymer material, which slowly biodegrades [9]. In this research PVA was a precursor to composite nanofibres synthesis and is composed of poly(vinyl) alcohol (PVA) copper acetate (CuOAc) and acetic acid ($CH_3COOH$). To optimize the process of electrospinning from solution various solvents were tested, and their effects on the properties and structure of the micro and nanofibres with inorganic additives were investigated [10,11].

## 3. Experimental procedure

The main problem being investigated of this research is the impact of electrospinning process parameters and the polymer solution applied on the diameter shape and properties of obtained polymer micro and nanofibers. Fabrication of the polymer fibres was performed with Electro-Hydrodynamic Atomization 2.2D-500 device made by flow Nanotechnology Solution. The electrospinner consists of three main components: a collector, a spinneret and a power supply. The polymer solution is contained in a syringe, which is connected to the spinneret. A controllable and constant rate of solution introduction can be obtained through the use of a syringe pump. At the nozzle end of the spinneret a drop of polymer solution appears when a high voltage is applied. Due to the high voltage applied charges are evenly distributed over their surface. Two major forces interact on the droplet, which distorts into a Taylor cone. A collector is placed under the spinneret, which acts to attract the solution [1, 9-11].

The morphology of the obtained fibres was investigated using a SEM SUPRA 35 scanning microscope by ZEISS with accelerating voltage of 3-25 kV. The observations were made with the magnification of 1000 to 100 000 times in order to determine the influence of the applied solutions and fabrication conditions on nanofibre diameter, their spatial arrangement and formation of defects. Digital Micrograph365 software was used in the research [6,7].

Table 1.
Electrospinning process parameters for 7 wt% solution of PEO in $H_2O$

| Sample | Distance [cm] | Flow rate [ml/h] | Voltage [kV] |
|---|---|---|---|
| Sample 1 | 10 | 0.5 | 7 |
| Sample 2 | 25 | 0.9 | 7 |

Table 2.
Electrospinning process parameters for 7 wt% solution of PEO in DMSO and $CH_3Cl$

| Sample | Distance [cm] | Flow rate, [ml/h] | Voltage [kV] |
|---|---|---|---|
| Sample 3 | 10 | 0.5 | 7 |
| Sample 4 | 25 | 0.9 | 12 |

Three solutions of PEO and one of PVA, each with a different solvent were prepared. Necessary concentrations were measured and mixed to obtain a homogenous solution of polyethylene oxide and a solvent: water (Table 1),

DMSO (dimethyl sulfoxide) and chloroform in ratio 1:1 (table 2), methanol and chloroform in ratio 1:1 (Table 3). For all PEO solutions the polymer concentration was 7 wt%. In case of solution of PVA in CuOAc and EtOH, the percentage ratio of components was approximately of 20%, 27%, 53% (table 4). Each solution was then placed in a syringe for electrospinning and processed. Parameters for each process are presented in Tables 1-4.

Table 3.
Electrospinning process parameters for 7 wt% solution of PEO in $CH_3OH$ and $CH_3Cl$

| Sample | Distance [cm] | Flow rate [ml/h] | Voltage [kV] |
|---|---|---|---|
| Sample 5 | 10 | 0.5 | 7 |
| Sample 6 | 25 | 0.9 | 7 |

The variable parameters in the performed experiments are distance between the nozzle and the ground collector, feed rate of solution and voltage between nozzle and collector. The fibres were deposited on previously prepared numbered sections of aluminium foil to better facilitate their transport, SEM sample preparation and imaging. The duration of one attempt was about 15 minutes.

Table 4.
Electrospinning process parameters for 20 wt% of PVA solution in CuOAc and EtOH

| Sample | Distance [cm] | Flow rate [ml/h] | Voltage [kV] |
|---|---|---|---|
| Sample 7 | 10 | 0.2 | 20 |
| Sample 8 | 10 | 0.5 | 20 |
| Sample 9 | 10 | 0.2 | 30 |
| Sample 10 | 10 | 0.5 | 30 |

## 4. Analysis of the results

Based on the investigations performed on the fibres obtained from the previously described solution and with the process parameters listed in the tables 1-4 there is a significant influence from solution viscosity and process parameters on the morphology and diameter of the fibres obtained. Because of limitations in scanning electron microscopy, in order to analyse the nanofibres a layer of vacuum deposited gold was applied in a vacuum sputter coater. After sputtering the samples were attached to the SEM sample tables using carbon adhesive tape. Additionally histograms of fibres diameter distribution were prepared for each samples based on the measurements performed with aid of Digital Micrographs analysing tool. Results of the performed observations are presented on the following photographs and diagrams (Fig. 1-10).

The morphology investigation results confirm the influence of process parameters on the shape and dimensions of obtained samples. Figure 1 shows the SEM micrographs of fibres made from solution of PEO in $H_2O$. The distance between the nozzle tip and the collector was 10 cm, and the flow rate of solution was 0.5ml/h. The same solution processed with significantly different conditions, the distance 25cm and speed of flow rate of 0.9ml/h allows to produce microfibers presented on the Fig. 2. There are no visible differences in the observed morphology of fibres, the only difference concerns density of fibres with beads and the beads diameter.

During the electrospun process of PEO with DMSO and chloroform solution it has to be noted that the process continuity is frequently interrupted and the accelerating voltage have to be increased up to 12 kV. After changing of distance and flow rate the creation of Tyler cone was interrupted. Flow of solution was impeded because solvent began untimely evaporates, and particles of polymers were deposited on nozzle sides, when the flux is much more narrow. Figure 3 and 4 show the image of selected samples.

Next PEO solutions were made with chloroform and methanol. Results of electrospun fibres morphology observation for the solution of PEO in chloroform and methanol are presented on a Figure 5 and 6. Taking into account results of previous experiments the aim was to reduce density and viscosity of the solution. However even for those solutions interruption of process was observed which was affected by too low flow rate. As a results two type of fibers were created with diameter of several microns and dozens of microns. After distance and flow rate change process becomes stable and the results are presented on Figure 6.

To compare morphology and diameter of obtained from PEO fibres, the electrospun process of fibers production from PVA in CuOAc and EtOH as a solvent was performed. Again parameters of the electrospinning process, which were varied, are flow rate and voltage, shown in table 4. The results of morphology observation and measurements of fibres diameter are shown on Figures 7-10 and Table 5.

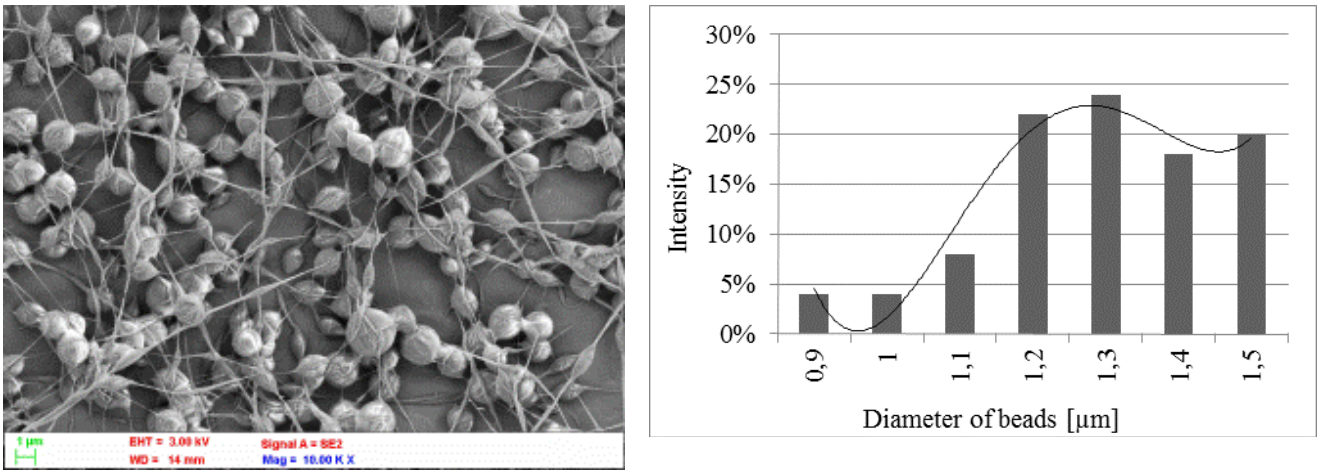


Fig. 1. Fibers with beads- Sample 1: a) morphology of the fiber (SEM), b) results of the diameter measurements

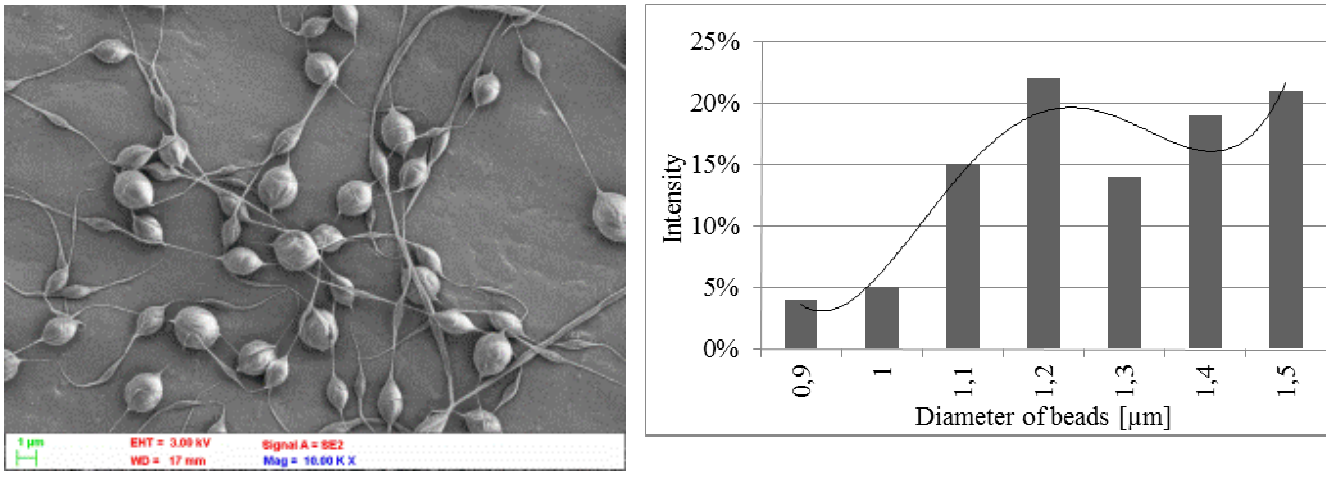


Fig. 2. Fibres with beads- Sample 2: a) morphology of the fiber (SEM), b) results of the diameter measurements

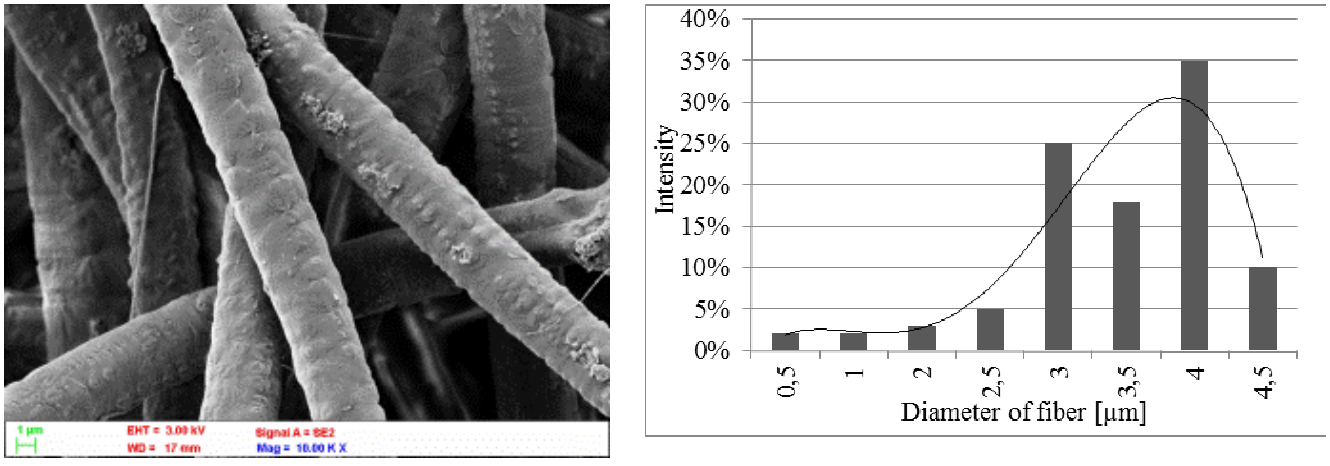


Fig. 3. Microfibres - Sample 3: a) morphology of the fibers (SEM), b) results of the diameter measurements

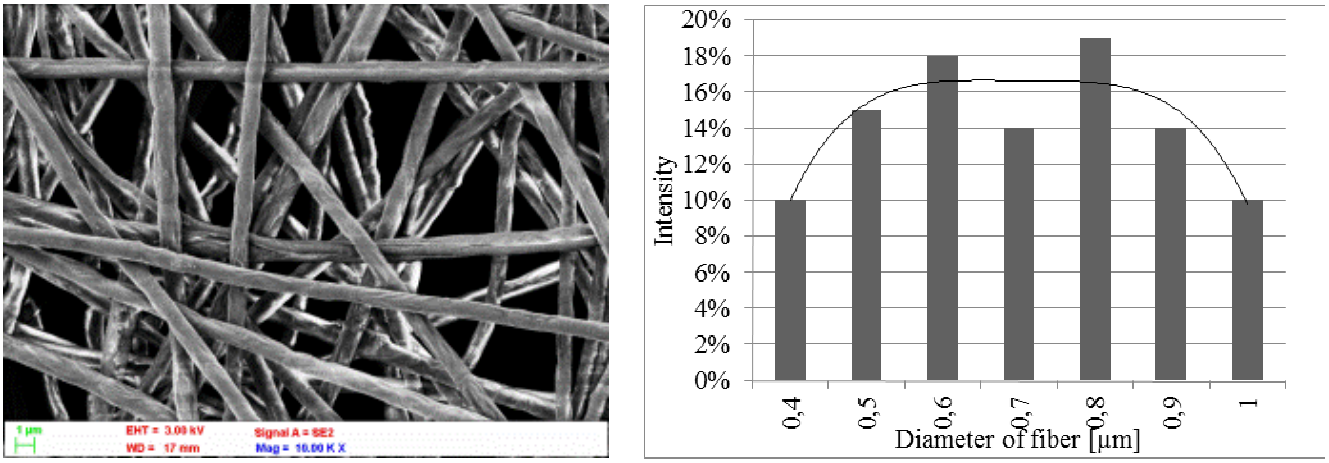


Fig. 4. Microfibres - Sample 4: a) morphology of the fibers (SEM), b) results of the diameter measurements

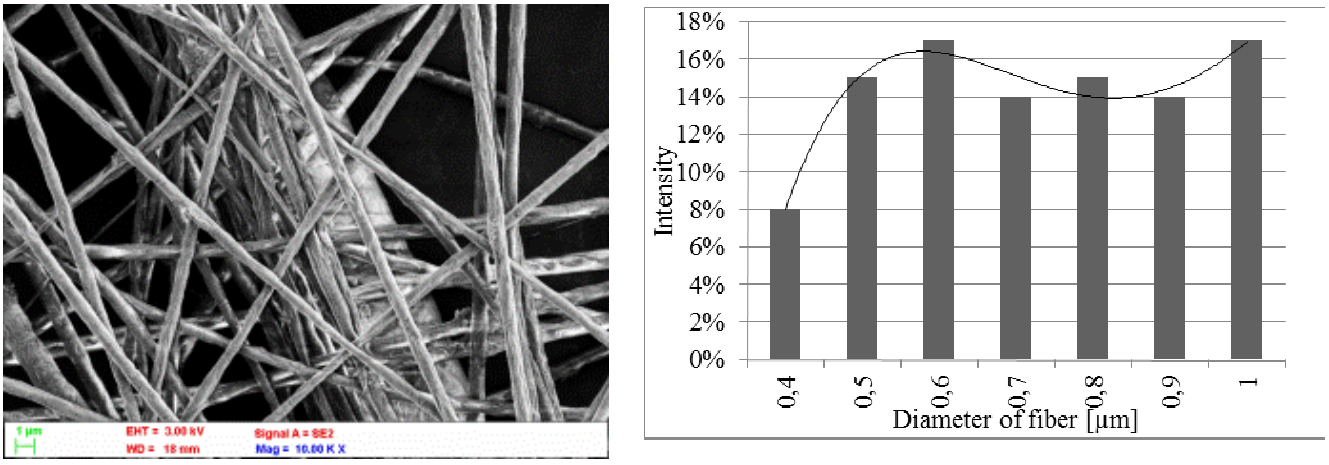


Fig. 5. Microfibres - Sample 5: a) morphology of the fibers (SEM), b) results of the diameter measurements

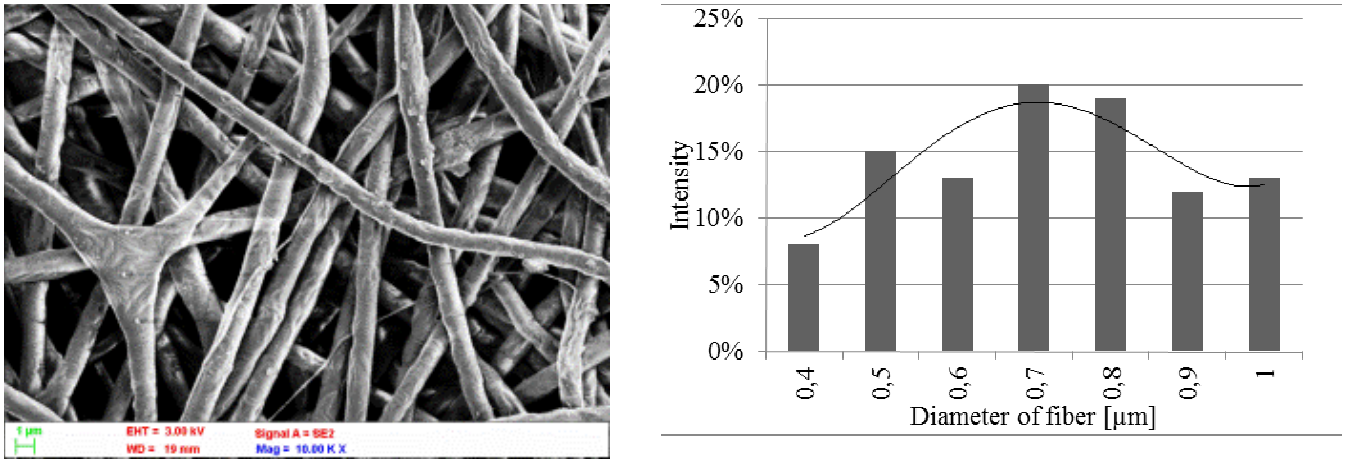


Fig. 6. Microfibres - Sample 6: a) morphology of the fibers(SEM), b) measurements of the diameter

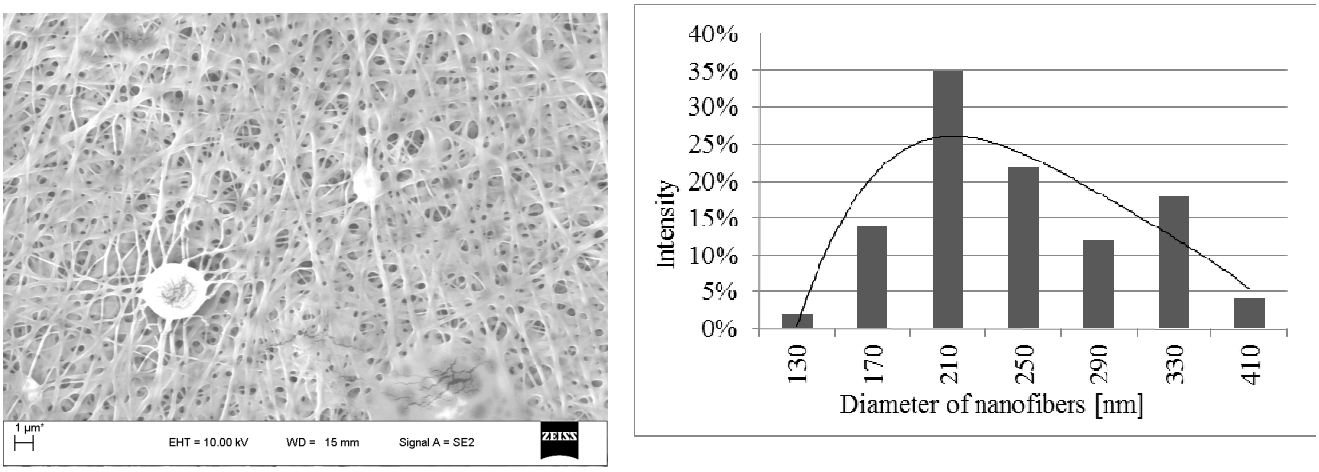


Fig. 7. Nanofibres - Sample 7: a) morphology (SEM), b) measurements of the diameter

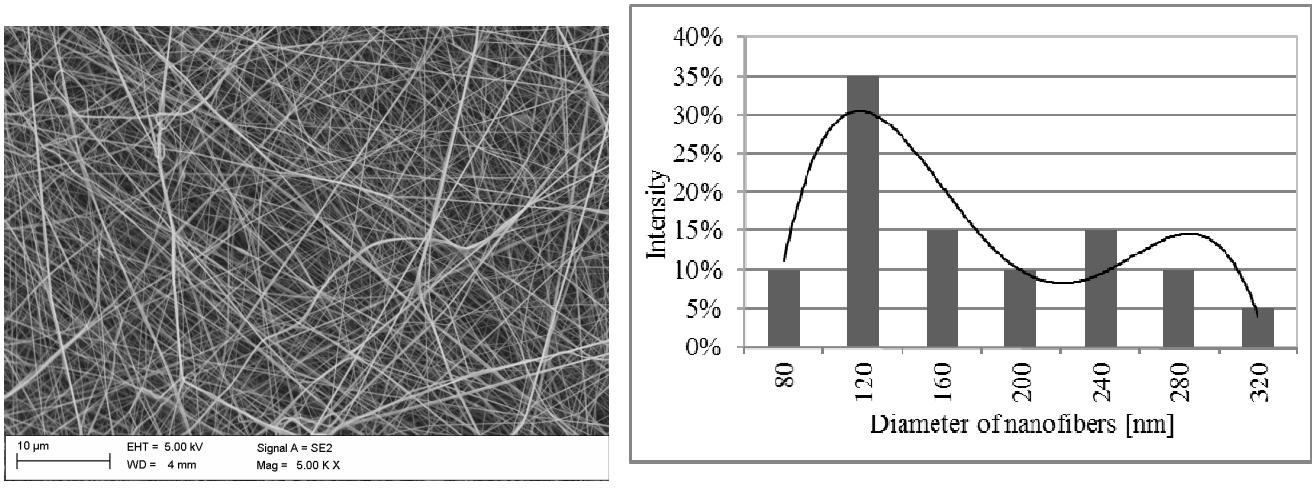


Fig. 8. Nanofibres - Sample 8: a) morphology (SEM), b) measurements of the diameter

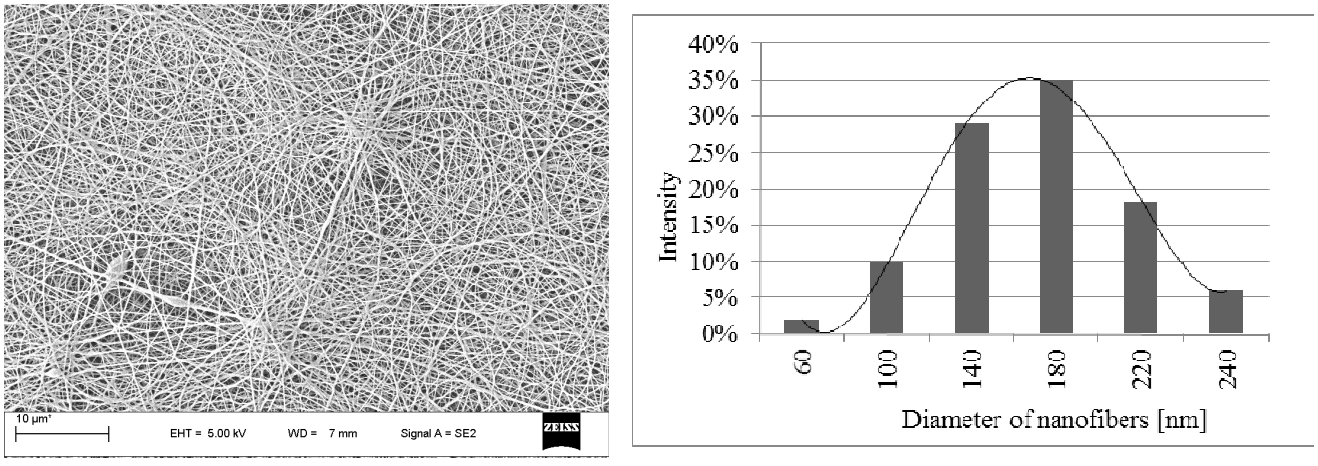


Fig. 9. Nanofibres - Sample 9: a) morphology (SEM), b) measurements of the diameter

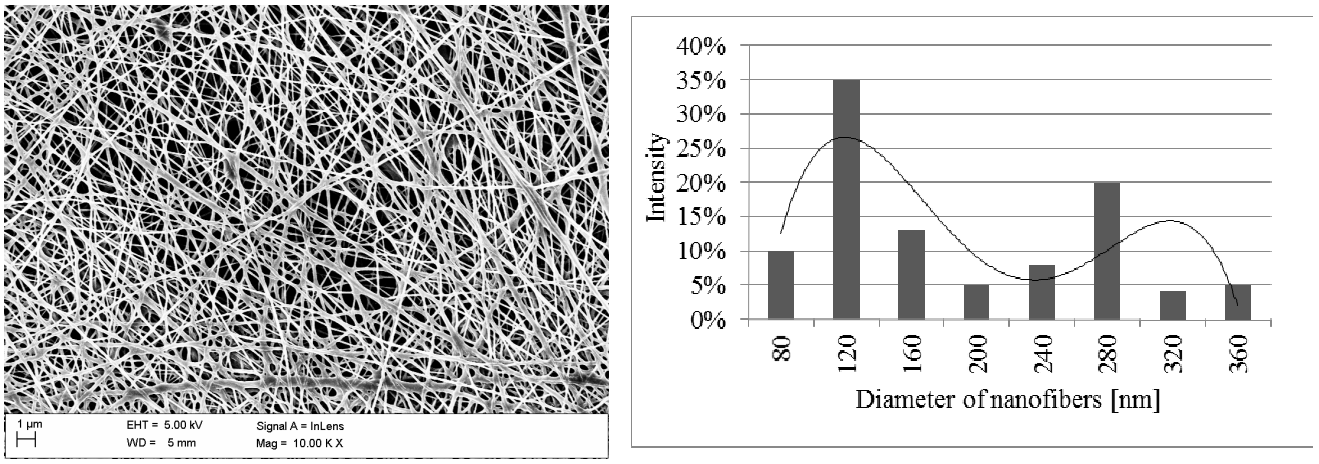


Fig. 10. Nanofibres - Sample 10: a) morphology (SEM), b) measurements of the diameter

Table 5.
The average of the diameters of the obtained fibres

| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 | Sample 8 | Sample 9 | Sample 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Diameter | 1.29µm | 1.33 µm | 9.66 µm | 0.7 µm | 0.72 µm | 0.72 µm | 235 nm | 180 nm | 165 nm | 155 nm |

## 5. Summary

Results presented for the PEO solution in water shows that the fibres morphology is connected with beads creation independent of the process parameter used in the experiment. This may be resulting from several factors: a low viscosity or high surface tension of the solution. The average thickness of the beads ranges from 1.1 to 1.4µm, while the fibres range from 200 to 500nm.

For the PEO dissolved in DMSO and chloroform Tyler cone formation was not observed and solution was found to fall down vertically, possibly due to low voltage applied for this solvent or too low solution flow. The fibre diameters were observed to fall within the range of 4 to 21µm.

For the PEO in methanol and chloroform a significant change was made in respect to the distance between the nozzle and collector. Changing the length of stream and volatility of the solvent influenced the shape of the fibres and internal solution load. For shorter distances the process was unstable, influencing fibre shape and the morphology. For of the fibres created from a distance of 25cm can be seen gradual stabilization of the process that indicates assignment of the optimal process parameters. Note the similarity in fibre diameter measurements, which in all cases are in the range of 0.5 to 1 µm.

Other parameters, which also can be varied while environmental parameters such as temperature and moisture and all these variables, can influence the electrospun nanofibres. The reason of the nanofibres merging in Sample 7 is probably too small distance between the electrodes for applied solution flow and voltage. The solution had evaporated on the road between the nozzle and the collector.

With the increase of voltage at the nozzle and the collector there reducing the average of diameter of the obtained nanofibres. The lowest average diameter at 155nm occurs in the case of Sample 10, when the voltage is highest (30 kV). The most even distribution of diameter of the nanofibres occurs in the Sample 8, when the voltage was 20kV.

PVA matrix composite nanofibres without visible defects in the form of beads and blur was achieved only in the case of samples 7-9.

During the electrospinning process, the liquid spurt was stable only in the case of sample 7. During the

producing of other samples liquid spurt was unstable or occurred multispurt.

The obtained results show the influence of applied solution and process parameters on the morphology of the nanofibers.

## Acknowledgements

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## Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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