THE INFLUENCE OF PRODUCTION PARAMETERS ON THE MORPHOLOGY OF NANOFIBER MEMBRANES

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Abstract

Development of new materials is still growing up. The relatively new materials are nanofibers membranes. These fabrics are very popular due to their properties, which primarily depend on the structure of the material. This structure may be affected by several parameters. Setting of production parameters of the spinning device have a major impact on the structure of the fabric. The analysis of this effect is the main goal of this work.

In this paper nanofiber textiles were manufactured by using the device Nanospider™ NS LAB 500 S (Elmarco, CR). As the main spinning polymer was used polyvinyl alcohol (PVA). We created 15 types of textile where technological parameters were changed. This work contains two experimental parts. In the first one, we analyzed the effect of voltage, distance of the electrodes and the solution concentration. There were not achieved fundamental changes in the structure of the fabric. In the second experiment, we tested the effect of changes of the electric field to change the structure of the resulting nanofiber membranes. The structure was analyzed using a scanning electron microscope Tescan Maia 3. In this experiment, we achieved significant changes in structure and thus we demonstrated the significant influence of adjustment of the electric field on the final fabric structure.

Keywords: Nanospider, nanofiber membrane, structure, production parameters

1. INTRODUCTION

Nowadays, the searching of new materials in civil engineering is very popular. Especially the use of composites. Materials based on a polymer are very desirable elements because they are recyclable. In our paper we study the morphology of nanofiber membranes made from different polymers. These membranes were produced on the device called NanospiderTM which operates on the principle of an electrostatic spinning. Nanofiber textiles have a great potential for application in many branches of technology thanks to their structure [1]. The morphology of the membrane is very complicated [2]. It is a chaotically organized structure of polymer fibers. Diameter of the fibers ranges from tens of nanometers to micrometers [3]. Due to very small diameter of fibers, the fabric has a huge surface area which can be used for example in air conditioning. Moreover, the nano fiber fabrics are open to diffusion and may possess hydrophobic properties. In other cases, the fabric may be used as a scaffold for active particles, which can provide protection of building surfaces against molds [4].

All these properties of nanofiber membranes strongly depend on their structure. There is a number of studies which deal with the relationship between the structure of the textile and production parameters during the spinning process. The main parameters of the spinning process, causing changes in the structure of nanofiber membranes, are voltage and viscosity of the polymer solution [5, 6]. In 1971 P. Baumgarten established the dependence of the diameter of the fiber on the viscosity of the solution [5]. Further information about the possibility to influence the structure of the nanotextile can be found in the work of L. Lorand [6]. He proved that there exists a relationship between the fiber diameter and the temperature of the polymer solution. The higher temperatures lead to smaller diameter of fibers. Moreover, he proved that the diameter of the fibers decreases with increasing voltage [6]. Another parameter that changes the structure of the fabric could be concentration of polymer in a solution. The effect of concentration on electrospinning process was tested in [7]. It was observed that the low concentration leads to the electro spraying. Furthermore, in this paper the influence of voltage on the final shape of the fibers has been studied. It was shown that with decreasing voltage fibers are straighter. Further works [8, 9] correlate with the previous results.

All of these studies were performed on a conventional electrostatic spinning apparatus. In our case, we used the device Nanospider NS LAB 500S, where the method of producing nanofibers fabric is different. The aim of this work is to demonstrate that here the production parameters also have very important impact on the resulting structure of nanofiber membranes.

2. MATERIAL AND METHODOLOGY

In this work was used a polymer solution of polyvinyl alcohol (PVA) for producing a nanofiber membrane. All fabrics analyzed in this work were made in the center for nanotechnology in Czech Technical University in Prague. The polymer solution was prepared from the following additives: 75 g Sloviol R16 (Fichema, CR, SLoviol R16, 16% PVA), 0.88 g glyoxal, 0.6 g 80% phosphoric acid (Sigma Aldrich USA). The solution was completed with demineralized water to 100 g. After the preparation of the suspension, solution was homogenized by using ultrasonic and magnetic stirrer. Afterwards the solution was put in the Nanospider where the production parameters were changed for fabrication of different types of nanofiber membranes. The resulting fabric was stabilized by heating to 140 °C for 10 minutes, which caused the textile stability in contact with water.

The final fabrics were analyzed by using a scanning electron microscope Tescan MAIA 3 at the Institute of Physics, CAS in Prague.

Production of textiles was performed in two series of experiments. The production parameters of the first series of the experiment are shown in the **Table 1.**

Table 1 Production parameters of nanofiber membranes in the first experiment

Sample	Polymer	Speed of substrate [m/min]	Distance of electrodes [mm]	Voltage [kV]	Concentration of solution [%]
A	PVA	0.13	100	70	10
B	PVA	0.13	110	70	10
C	PVA	0.13	120	70	10
D	PVA	0.13	130	70	10
E	PVA	0.13	140	70	10
II	PVA	0.13	110	70	12
III	PVA	0.13	110	70	8
c1	PVA	0.13	140	68.2	10
c3	PVA	0.13	140	71.8	10
c5	PVA	0.13	140	75.2	10
c7	PVA	0.13	140	78.8	10
c9	PVA	0.13	140	82	10

3. THE FIRST SET OF EXPERIMENTS

We planned the first set of experiments based on information available in the literature, where mainly the influence of the voltage and the concentration of the solution were studied. In our experiments the impact of the distance of the spinning electrode on the resulting structure was tested. Limit values of the voltage were experimentally determined. If we use a low voltage, the production process completely stops. On the other hand, if we use too high voltage, it may cause an electrical breakdown. The lowest voltage at which we observed the nanofibers production was 68.2 kV. The highest safe value of voltage was 82 kV. However, these values are not fixed. They mainly depend on the humidity of the ambient air. After creating of fabrics, they were stabilized and the final structure has been mapped using an electron microscope. Difference in structures between the samples produces under the lowest and highest voltage is shown in the **Figure 1.**

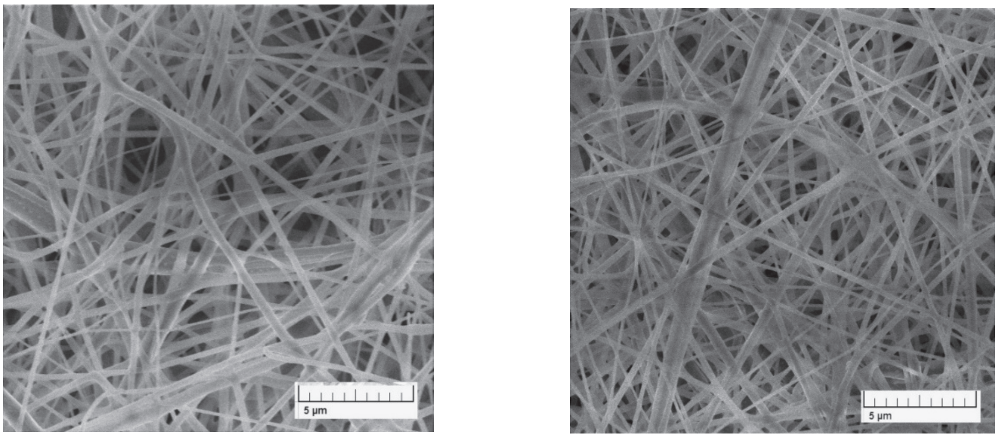


Figure 1 Comparison of the structure of nanofiber membranes produced with different spinning voltage. To the left is sample c1 (lowest voltage 68.2 kV), to the right is sample c9 (maximum voltage 82 kV)

In the next stage of the experiment, the distance between cylindrical rotary electrode and movable collector for collecting final fabric was changed. The limit values of the distance were determined in the same way as the limit values of the voltage. The shortest distance between the electrodes was achieved during production of sample A and was 100 mm. The longest distance of 140 mm was achieved in sample E. Values less than 100 mm caused electrical breakdown, on the other hand values higher than 140 mm caused the device to stop production of fibers. The difference of structure of nanofiber membranes caused by varying distance between the electrodes is shown in the **Figure 2**.

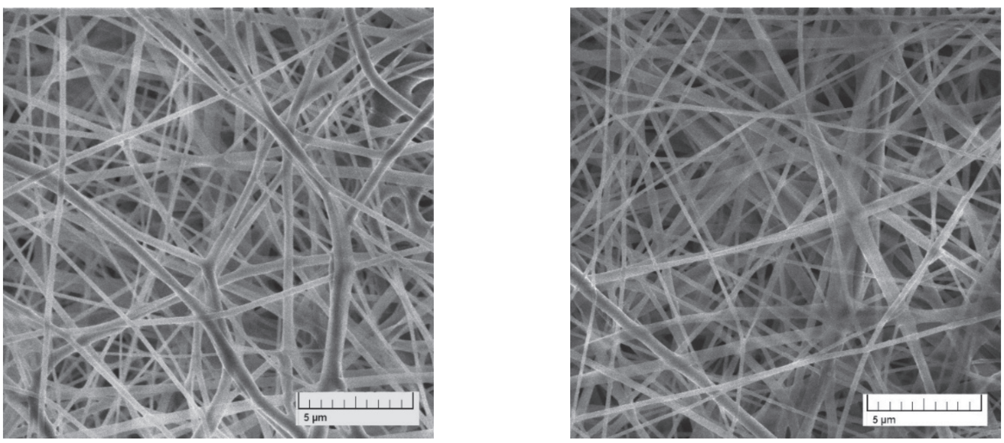
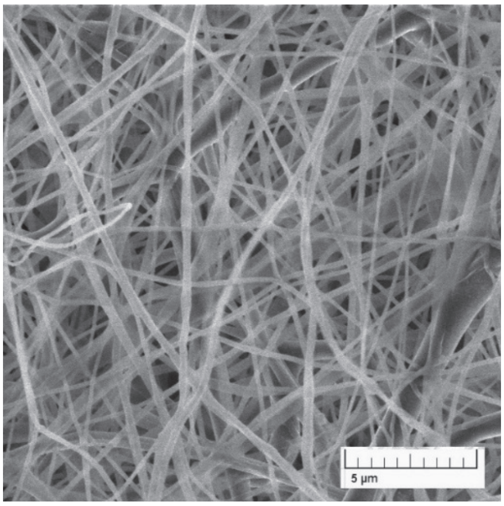


Figure 2 Comparison of the structure of nanofiber membranes produced with different distance between electrodes. To the left is sample A (minimal distance of 100 mm), to the right is sample E (maximal distance of 140 mm)

In the last stage of experiment the impact of solution concentration on the structure of nanofiber membrane was examined. We achieved different viscosity of solution by change of concentration (8%, 10%, 12%). The difference of structure of nanofiber membranes caused by different concentration of solution is shown in the **Figure 3.**



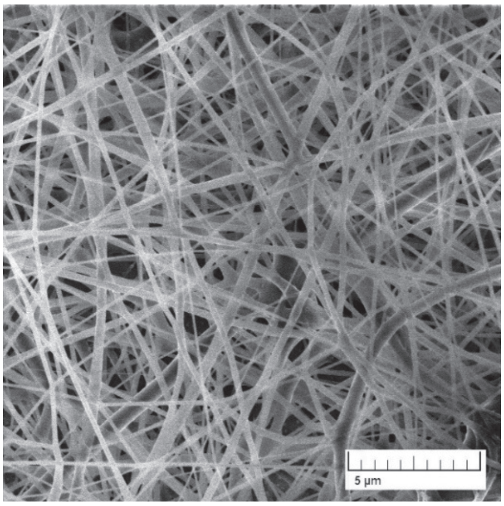


Figure 3 Comparison of the structure of nanofiber membranes based on different concentration of PVA solution. Left sample II (highest concentration of 12%), right sample III (lowest concentration of 8%)

4. RESULTS OF THE FIRST SET OF EXPERIMENTS

Within the frames of the first set of experiments we have studied the dependence of the structure of polymer nanotextile on three parameters of the production process: the voltage, the distance between the electrodes, and the concentration of the polymer solution. Contrary to similar experiments conducted by other authors ([5-9]) we have not observed significant changes in the structure. However, this fact could be possibly explained by differences in manufacturing process. In our work we have used nanotextiles produced by Nanospider device, while the cited works studied the materials produced by traditional electrospinning. Thus, the relatively small variations of the nanotextile structure in our experiments may suggest a greater stability of Nanospider technology.

5. THE SECOND SET OF EXPERIMENTS

As stated above, in the first set of the experiments we tried to vary the voltage in the maximum possible range in order to obtain observable changes in material structure. On the other hand the structure of the fabric is controlled primarily by interplay of electrostatic energy with the surface tension of the polymer solution. The former is determined by the electric field, not the actual voltage. Thus, in the second set of experiments our goal was to achieve the highest possible variations in electrical field and not just simple applied voltage.

For calculation of the electric field we use the following formula:

$E = \frac{U}{d}$, where U is the applied voltage and d stands for the distance between the electrodes.

It is easy to check, that in the first set of the experiments this ratio remained almost constant. In order to achieve larger variations of the electric field we have produced a new set of fabrics. Production parameters of these fabrics are shown in the **Table 2**. It should be noted that we have managed to achieve higher critical values of voltage and distance of electrodes. This could be possibly explained by the lower air humidity during production of the second set of textiles.

Table 2 The production parameters in the second set of experiments

Sample	Polymer	Speed of substrate [m/min]	Distance between electrodes [mm]	Voltage [kV]	Electrical field [kV/mm]	Concentration of solution [%]
E_{min}	PVA	0.13	210	50	0.24	10
E_{avg}	PVA	0.13	150	70.3	0.47	10
E_{max}	PVA	0.13	100	78	0.78	10

As it is clear from the **Table 2** in this set of the experiments we have managed to achieve high variation of the intensity of the electric field. The highest achieved intensity is more than three times stronger than the lowest one. After the production and stabilization of the fabric, the surface structure of the samples was studied by electron microscopy. Comparison of the individual structures of the fabric is shown in **Figure 4.**

a)

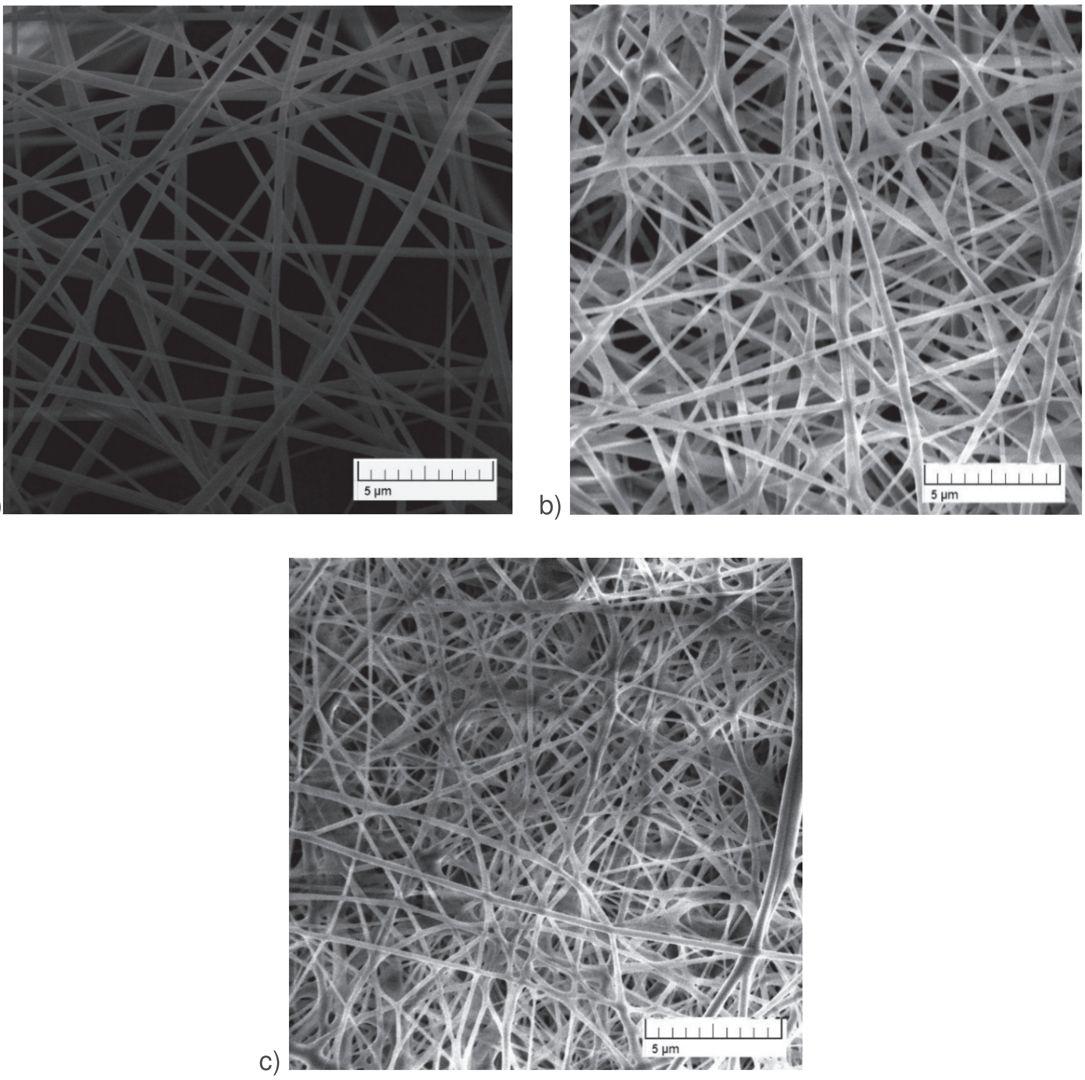


Figure 4 Comparison of the structure of nanofiber membranes based on different electrical field.
a) the lowest electrical field Emin 0.24kV/mm,
b) the average electrical field Eavg 0.47 kV/mm,
c) the highest electrical field Emax 0.78 kV/mm

6. RESULTS OF THE SECOND SET OF THE EXPERIMENTS

The electric field has a considerable influence on the structure of the fabric. At lower intensities of electric field the fibers are produced at lower rate which causes less surface density of the resulting fabric. Higher intensities lead to production of nanotextiles with higher surface density. The electric field also influences the curvature of the fibers. We have found that curvature of fibers produced under higher values of the electric field is larger. Moreover, the diameter of the fibers is decreasing with growing electric field.

7. CONCLUSION

In this work we have analyzed the surface structure of 15 types of textiles, produced by Nanospider NS LAB 500S device under different production conditions (voltage, distance between electrodes, and concentration of the polymer solution). We have found that the electric field strongly affects the structure. However, the value of the voltage itself is not enough to calculate the electric field, and, thus, does not provide enough information about the technological process. The information about the distance between the electrodes is just as important as the voltage. On the other hand, in the articles devoted to electrospinning process the electric field is usually specified by just a single parameter - the voltage. Our work shows, that it is always necessary to provide information about both the voltage and the distance between the electrodes.

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REFERENCES

[1] KIM, H. G. and KIM, J. H. Preparation and properties of antibacterial Poly (vinyl alcohol) nanofibers by nanoparticles, *Fibers Polym.*, vol. 12, no. 5, pp. 602-609, Aug. 2011.

[2] HAVRLIK, M., & SVESHNIKOV, A. Initial study of structure of nanofiber textiles and the creation of its model. *Paper presented at the NANOCON 2015 - 7th International Conference on Nanomaterials - Research and Application*, Conference Proceedings, 287-291. Nov. 2015.

[3] ANDRADY, A. L. Science and Technology of Polymer Nanofibers. *John Wiley & Sons*, 2008.

[4] HAVRLIK M., RYPAROVÁ P. Protection of Wooden Materials Against Biological attack by Using Nanotechnology, *Acta Polytech.*, Vol. 55, No. 2, pp. 101-108, 2015.

[5] P. K. Baumgarten, Electrostatic spinning of acrylic microfibers, J. Colloid Interface Sci., vol. 36, no. 1, pp. 71-79, May 1971.

[6] LARRONDO, L. and MANLEY, J. R. St. Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties, *J. Polym. Sci. Polym. Phys. Ed.*, vol. 19, no. 6, pp. 909-920, Jun. 1981.

[7] HUANG, Z. M., ZHANG, Y.-Z., KOTAKI, M., and RAMAKRISHNA, S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites, *Compos. Sci. Technol.*, vol. 63, no. 15, pp. 2223-2253, Nov. 2003.

[8] LI, Z. and WANG, C. Effects of Working Parameters on Electrospinning, in One-Dimensional nanostructures, *Springer Berlin Heidelberg*, pp. 15-28., 2013.

[9] YUAN, X., ZHANG, Y., DONG C. and SHENG J. Morphology of ultrafine polysulfone fibers prepared by electrospinning, *Polym. Int.*, vol. 53, no. 11, pp. 1704-1710, Nov. 2004.