# Study of the Influence of Electrospinning Parameters on the Structure and Morphology of Polyvinyl Alcohol Nanofibers

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*The paper presents the influence of some parameters involved in needleless electrospinning technology on the structure and morphology of polyvinyl alcohol nanofibers. Based on theoretical and practical aspects of the nanofibers obtained by needleless electrospinning technology and of the polyvinyl alcohol characteristics, were determined the areas of polymer concentration and the characteristics of the applied voltage, involving an electrospinning device equipped with a rod spinning electrode with a diameter of 8 mm and a lenght of 170 mm. The applied voltage to the rod spinning electrode was between 0-40 kV, domain in which the influence on the elongation level of the jet can be felt, with a direct action on the surface morphology of the nanofibers and on the relaxation time of the polymer, respectively. Regarding the concentration of polyvinyl alcohol aqueous solution, it was found that using low concentrations (5% wt), no matter what the value of the voltage is, instead of nanofibers droplets are formed and the electrospraying process appears. Instead, increasing the solution concentration causes a fusion of the droplets in nanofibers. Because droplets modified from spherical to spindle-like form and the distance between droplets increases with increasing viscosity, uniform nanofibers with larger diameters can be obtained. The range of concentrations where uniform nanofibers can be obtained, without beads on the surface, is between 10% wt and 16% wt polyvinyl alcohol in water.*

*Keywords: nanofibers, needleless electrospinning on the rod, polyvinyl alcohol aqueous solutions, the applied voltage on the rod, solution concentration, applications of the nanofibers*

Among the main technologies, developed up to the present, for obtaining nanofibers (drawing, template synthesis, phase separation, self assembly), electrospinning is the most efficient from the point of view of productivity [1]. The process of electrostatic forces to form synthetic fibers is known for more than 100 years. This uses a power source in order to introduce a specific polarity in a polymeric solution or in the melting form, which is then attracted to a collector of opposite polarity. If attraction to the collector is much stronger than electrostatic repulsion of the same polarity in the solution, forming the tip jet shape changes from rounded to the meniscus form. At a critical point, a jet erupts from the surface of the liquid. This point of eruption is known as the Taylor cone. Once the electrostatic forces overcome the surface tension of the polymer solution at the nozzle tip, a jet is drawn from the tip of the nozzle. The jet elongates, it gets into the atmosphere while solvent is evaporating and the produced nanofibers are deposited on the collector. Resulted fibers have diameters typically in the range of 100 nm-500 nm, with controlled orientation, adaptable to different types of polymers and uses both in laboratory and industrial scale [1].

So far, two methods are known for obtaining nanofibers using high voltage, namely: *needle electrospinning method* and *needleless electrospinning method*. Both methods seem to be different, however they are based on the same electrospinning mechanism.

By using needle electrospinning technique (fig. 1), polymeric solutions are easyly spinnable and controllable for obtaining the desired products, there is only one jet per needle and the spinning area is very small (0.5-1 mm$^2$).

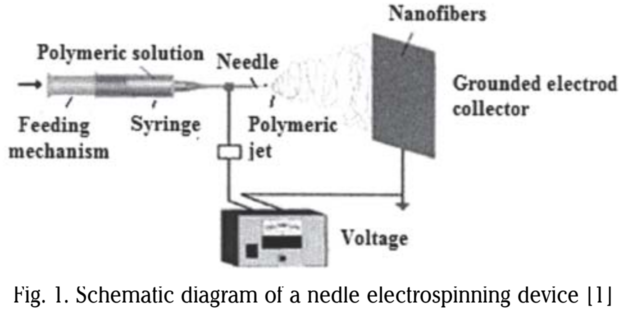


Fig. 1. Schematic diagram of a nedle electrospinning device [1]

Schematic diagram of a needle electrospinning device (fig.1) [1-4] consists of a syringe (a), a hollow needle (b), a feeding mechanism (c), a grounded collector electrode (d) and a high voltage (e). The solution is supplied through the capillary needle with a dosing pump at a constant flow rate which may be adjusted depending on several parameters. The collector of the nanofibres is positioned immediately below the needle, adjustable (300-1000 mm).

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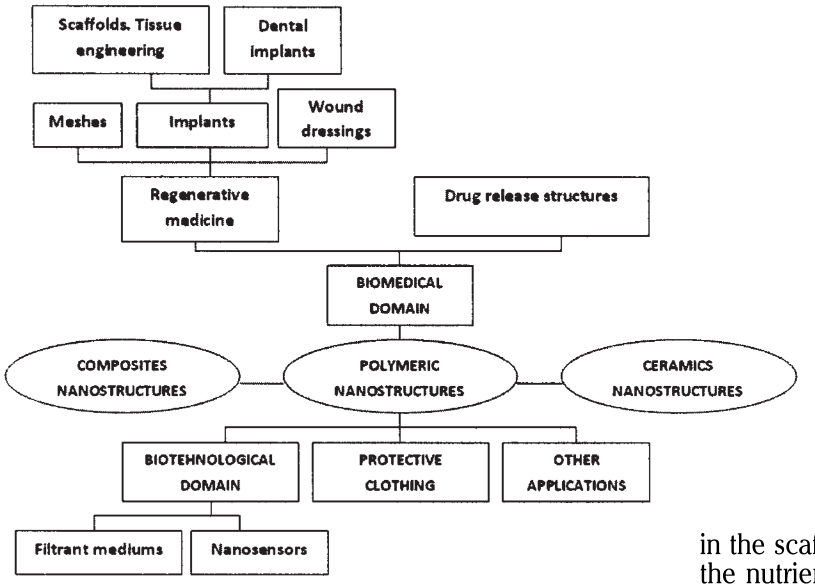



Fig. 2. Applications domains of electrospun nanofibers [6]

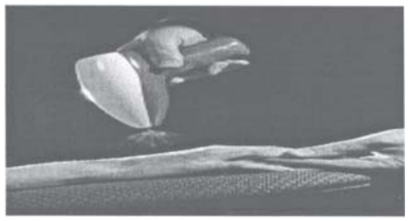


Fig. 3. Nanofibers for bandages [20-23]

Between the needle and a grounded collector, a voltage of the order of tens of kilovolts can be applied, causing the transformation of polymeric solution in an electrically charged polymeric jet, obtaining nanofibers and their deposition on the surface of the collector.

In order to commercialize the products resulted from electrospinning technology, emphasis has been given by the increasing of production capacity and the quality of nanofibers, promoting the needleless electrospinning technology, a procedure in which a relatively large number of polymeric jets (usually 3.000-4500 jets per one square meter of the surface of spinning electrode) are created spontaneously from a free surface of the liquid. Pioneering work was reported by [1], who used a magnetic fluid to agitate polymeric solution, in order to initiate the production of multiple jets from a flat surface of polymeric solution and therefore increasing the production of nanofibers. Another idea, described by [3, 5] is based on the fact that the jets are obtained even from free areas of the liquid, almost flat, resulting in to a massive production of nanofibers and a commercializing of technology under the Nanospider name. This technology describes the generation of multiple jets from an electric charged liquid on an horizontal cylinder slightly rotating.

Other advantages of the needleless electrospinning method are: there is no risk of obstruction of the needle; can be obtained a variety of polymeric nanofibers; can be used different materials substrates; controlled diameters of nanofibers; the nanofibers may have a certain uniformity, the desired quantity; there is the possibility to incorporate nanoparticles.

Electrospun nanofibers can be of polymeric, ceramic or composite nature. Each of these groups has a broad portfolio of applications (fig. 2) [6].

Tissue engineering is an innovative technology which combines the materials engineering, the cellular biology and the genetic engineering to get to the artificial tissues and to the organs such as skin, cartilages for joints, heart valves, bones. From biological point of view, almost all human organs and tissues are composed of structures with hierarchical organization at nanometric scale. There are several priority requirements, generally accepted for these nanostructures, respectively [7-22]: high surface area, high porosity (for cell migration), proper distribution of the pores which allow the growth both of the cells and of the tissues in the scaffold and which allow a proper conveyance of the nutrients and oxygen; biodegradability, non-toxicity, biocompatibility, interaction, positive adhesion with the human body, proliferation, migration; scaffold's architecture is very important, scaffolds with nano architectures have a greater surface area for the absorption of proteins; the equilibrium between the surface hydrophilicity and its hydrophobicity for cell attachment; proper mechanical force to support the growth of the new tissue, its form and tridimensional size.

The raw materials used for obtaining electrospun nanofibers can be natural or synthetic, of polymeric, ceramic or composite nature. These materials are selected according to the nature and structure of the tissue which follows to be regenerated. For soft tissue regeneration, by electrospinning can be processed polymers and for hard tissue regeneration can be utilized ceramic materials or composite structures which allow the incorporation of bioactive substances in distinct areas of the matrix. Most of the researches in this area focuses on the use of electrospun natural polymers. Natural polymers such as collagen, elastin, keratin, silk, chitosan, fibrin, gelatin, alginates and hyaluronic acid are ideal candidates for scaffolds. Of particular interest are materials of silk worm proteins and silk worm spider web due to their superior biocompatibility and combination of unique mechanical properties, strength and resistence. Major advantages of natural materials to synthetic ones are cell interaction and that are non-toxic degradation products.

The possibility of obtaining meshes from electrospun nanofibers is another practical application from the biomedical domain (reconstructed heart, blood vessels, peripheral vascular reconstruction) [17-19].

Another domain is that of textile compression (bandages, wound dressings, etc.). With the electric field, smooth nanofibers of biodegradable polymers can be sprayed directly on the wound to form a bandage of network nanofibers (fig. 3) [20-23].

According to [20-23] have been developed a series of bandages, which in preliminary tests, have shown a reduction in wound healing time from months / years in a few days / weeks. These bandages are obtained by wrapping polymeric ultrafine fibers, resulting in a very thin and elastic fabric, which takes the form of substrate, but does not stick to the wound. These bandages can be absorbed and may slow release drugs in the application area. Continue efforts using polymeric nanofibers membranes as medical bandages are still at an early stage, trying (Bowlin research group) to generate nanofibrous networks from fibrinogen, as a hemostatic bandage for

| Parameters | Effect on parameters |
|---|---|
| **Independent parameters** | |
| **Process parameters** | |
| Applied voltage (kV) | Decrease in fiber diameter with increase of the applied voltage |
| Types of the colectors, the distance between electrode-collector (mm), lenght of the jets (mm) | |
| **Ambiental parameters** | |
| Temperature (°C) | Decrease in fiber diameter with increase in temperature |
| Humidity %) | High umidity results in circular pores on the surface of the nanofibers |
| Pressure (atm) | |
| **Solution parameters** | |
| Molecular weight of the polymer (g/mol) | Increase of molecular weigh with reduction in number of beads and droplets |
| Solution viscosity (Pas) | Increase in fiber diameter with increase of viscosity |
| Polymer concentration (%) | Increase in fiber diameter with increase of concentration |
| Solution conductivity (mS/m) | Decrease in fiber diameter with increase in conductivity |
| Tensiunea superficială (mN/m) | High surface tension results in instability of jets |
| Relaxation time of the polymer | High viscosity of the polymeric solution (high concentration) with higher relaxation time |
| **Dependent parameters** | |
| Density of the cones ($m^{-2}$), life time of the jet (s), non-fibrous areaa(%), diameters of the nanofibers (nm) | |

**Table 1**
ELECTROSPINNING PARAMETERS AND THEIR EFFECTS ON THE STRUCURE AND MORPHOLOGY OF THE NANOFIBERS [35]

the wound. Fibrinogen, which can be found in blood plasma, plays a key role in wound healing process.

With regard to the drug release structures, obtaining of electrospun polymeric nanofibers is a current concern of specialists. In a controlled release system, the active substance is loaded into a "messenger" and then is released at a controlled speed [22]. The basic features that promote the use of nanofibers in this biomedical application are [23-29]: high surface area which leads to an effective drug release; the ability to incorporate a large number of drugs within nanofibers; high porosity and small pore size, interconnected structure of the pores; nanofiber diameter: 100-500 nm; weight: 0.05 to 5 g/m$^2$; allow controlled drug release at a constant speed as much as possible over long periods of time, adjusted according to the domain of application; a controlled release only on the desired part of the body; biocompatibility; permeability; non-cytotoxicity [25, 28, 30].

Obtaining of filtering media is another well known application area:there are filters which incorporate electrospun nylon fibers for gas turbines, compressors and generators, and nanofiber filters for applications in automotive industry [1]. The main advantages of using the nanofibers filtering media as against the conventional classic ones are [27]: high separation capacity, excellent filtration properties, long life filter material, low investment costs, low power consumption.

Protective clothing impose some functional requirements dictated by environmental characteristics. It must provide the following characteristics: respirability; permeability to air and water vapors; strenght to exposure agents (thermal factors, chemical agents, etc.); high porosity but a very small pore size; high surface area [31].

Currently there are constant concerns for the integration of the electrospun nanofibers in other areas. For example, a company patented an electrospun nanofibrous material with an excellent capacity to absorb sound within a wide frecquency range, especially sound with the low frequency below 1000 Hz [32].

Nanocomposites obtained by electrospinning represent classes of materials in which components are combined so that at least one of its dimensions (length, width or thickness) has a value in the 1-100 nm range. Composite structures allow the incorporation of bioactive substances in different areas of the composite matrix. Priority characteristics of the composites in biomedical applications (tissue matrix support, dental restoration, controlled drug release structures, spinal implants) are mechanical wear resistance, corrosion resistance, flexibility, durability. The main disadvantages of composites are low tenacity, brittleness and some intrinsic fragility. The applications of nanocomposites are: automotive domain (tanks, protective bars, indoor and outdoor), construction domain, aerospace (fireproof equipment and high-performance components), electrical and electronical domain, supply packaging (containers and foil wrapping), high performance textiles (medical, protective, sports, typical clothing).

There are also known ceramic nanofibers made by electrospinning of ceramic precursors in the presence of a polymer, followed by calcination at high temperatures [33]. There is a wide range of tested applications of ceramic nanofibers obtained by electrospinning: chemical domain (catalysts, sensors), biomedical domain (bone tissue engineering), applications based on changing physical properties (information storage devices), other applications (aerospace) [34]. Ceramic nanostructures are essential materials for many applications, although only a few of them are commercialized due to the difficulties in maintaining their skills on a large scale.

## Experimental part

From the operational parameters which influence morphology and properties of nanofibers based on polyvinyl alcohol obtained by needleless electrospinning can be: solution concentration and voltage applied to the electrode.

It is known that diameter, structure and physical properties of nanofibers can be modified by the field of use, by controlling parameters which influence electrospinning process. The variables which contribute, as decision makers on the structure and external morphology of nanofibers, as well as the factors that affects electrospinning process and the resulted products are presented in table 1.

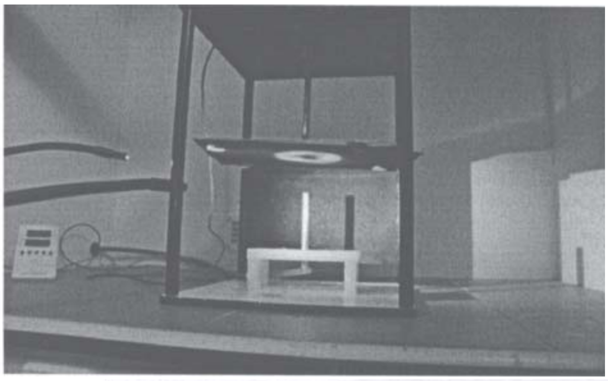


Fig. 4. Needleless electrospinning device equipped with a rod (Technical University of Liberec, Nonwoven Department)

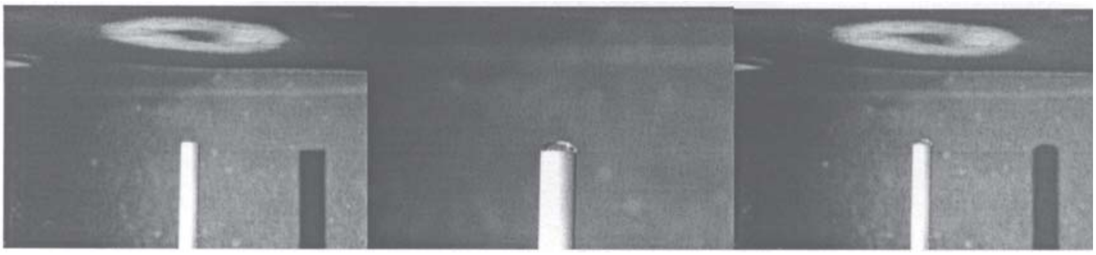


Fig. 5. The rod electrode (with and without polymeric droplet) and the metalic collector (Technical University of Liberec, Nonwoven Department)

**Table 2**
SURFACE TENSION $\gamma$ , DYNAMIC VISCOSITY $\eta$, MASS DENSITY $\rho$ AND KINEMATIC VISCOSITY $\nu$VALUES OF INVESTIGATED AQUEOUS PVA SOLUTIONS HEAVING CONCENTRATIONS FROM 5% wt TO 15% wt

| PVA weight concentration in % | Surface tension $\gamma$ [mN/m] | Dynamic viscosity $\eta$ [Pa s] | Mass density $\rho$ [kg/m3] | Kinematic viscosity $\nu$ [$m^2$/s] |
|---|---|---|---|---|
| 5% | 43.5 ± 0.1 | 0.01436 ±0.00003 | 994.7 ± 0.6 | 0.000014455 |
| 6% | 43.5 ± 0.1 | 0.0174 ±0.0001 | 1000.7 ± 0.4 | 0.000017521 |
| 7% | 43.5 ± 0.1 | 0.01897 ±0.00002 | 1002.3 ± 0.4 | 0.000018962 |
| 8% | 43.5 ± 0.1 | 0.0381 ±0.0001 | 1003.2 ± 0.3 | 0.000038114 |
| 9% | 43.5 ± 0.1 | 0.0532 ±0.0001 | 1004.1 ± 0.2 | 0.000053147 |
| 10% | 43.6 ± 0.1 | 0.1073 ±0.0002 | 1005.4 ± 0.4 | 0.00010686 |
| 11% | 43.7 ± 0.1 | 0.1220 ±0.0001 | 1005.8 ± 0.5 | 0.00012139 |
| 12% | 43.7 ± 0.1 | 0.2008 ±0.0001 | 1006.9 ± 0.4 | 0.00019944 |
| 13% | 43.7 ± 0.1 | 0.311 ± 0.002 | 1007.6 ± 0.4 | 0.00031045 |
| 14% | 43.8 ± 0.1 | 0.4994 ±0.0004 | 1008.5 ± 0.5 | 0.00049548 |
| 15% | 44.3 ± 0.1 | 0.5054 ±0.0004 | 1009.1 ± 0.1 | 0.00050109 |

*Electrospinning technology*

The experiments on the electrospinning of the PVA solution in water utilized a needleless electrospinning device. The electrospinner (fig. 4) is equipped with a rod electrode with a diameter *r* of 8 mm and a length *l* of 170 mm.

The electrode is mounted on an insulating stand. As a collector, it is used a metal device which collect nanofibers obtained from polymeric jet (fig. 5). The collector is supported by a mobile metal rod, that can be adjusted as required. As the collector substrates are used black paper, aluminium foil or nonwoven. The electrode is connected to the positive pole of the high voltage source while the collector is grounded. High voltage is applied to the polymeric solution so that the electric charge is introduced inside the fluid. When the charge inside the fluid reaches a critical time, polymeric jet erupt inside of the droplet, resulting in obtaining a Taylor cone. Once a critical voltage is exceeded, a charged jet ejects from the apex of the cone and deposits on the collection surface. Further increasing the electric field, a critical value is attained with which the repulsive electrostatic force overcomes the surface tension and the charged jet of the fluid is ejected from the tip of the Taylor cone.

All experiments were carried out with droplets having a volume of 1.5 mL, dose sufficient to cover the diameter of the rod. The shape of the polymeric solution droplet was carrefully controlled by the amount of polymer. For a better view of the electrospinning process, it was used a lighting device with two terminals which can be directed on the rod and the collector too. There isn't a special room to control temperature and humidity. Digital thermometer shows the temperature and atmospheric humidity, respectively. The ambient temperature was in the interval of 19 – 23°C and air humidity ranged within 35 and 51%. Specifications of the employed high voltage source is: 300 Watt High Voltage DC Power Supply with regulators; model number AU-60PO.5-L, output parameters 0-50 kV, 6 mA. It is important for the device to offer the possibility of repeated measurements and in particular compliance of the same initial conditions at the beginning of electrospinning. Each individual measurement is carried out from a new droplet. Photographic snapshots and video records of electrospun polymeric droplets were taken using Nikon camera Coolpix 4500.

*Materials*

Experiments uses aqueous solutions of poly (vinyl alcohol) Sloviol-R, with prominent molecular weight 130 000g/mol, having viscosity of 10.4 mPa s for 4% wt of an aqueous solution in distilled water. PVA has excellent film forming, emulsifying and adhesive properties. Because of excellent properties and biodegradability, PVA has found many uses (medical, cosmetic, pharmaceutic) and new ones are still being added. Recently, PVA became one of the most popular materials in electrospinning. Because of its non-toxicity and it can be dissolved easily in water so PVA can be used as a unique material, or PVA can be used in combination with other polymers which are not electrospinnable themselves, but have special functions for end use purposes [35].

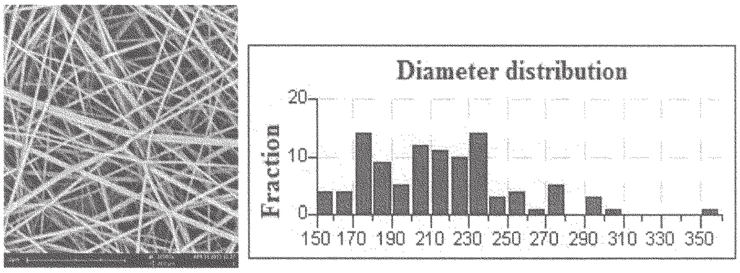
Concentrations of tested solutions were ranging from 5% wt up to 15% wt. Homogeneity of the solutions was ensured by keeping them on a magnetic stirrer Heidolph Vibramax 100 for three hours before each measurement. The values of surface tension, measured using Kruss tension-meter K12 and temperature were recorded for each concentration. To determine the polymeric solution density, 10 mL of the polymer solution was weighed in a Pentometer. All the measurements were repeated 5 times to obtain standard deviation values. The dynamic viscosity is determined for shear rates $\gamma \in (50, 600)$ $s^{-1}$. All values are measured at temperature of 20°C. All the aforementioned data of PVA solutions are introduced in table 2.

## Results and discussions

*Effect of applied voltage on the rod electrode*

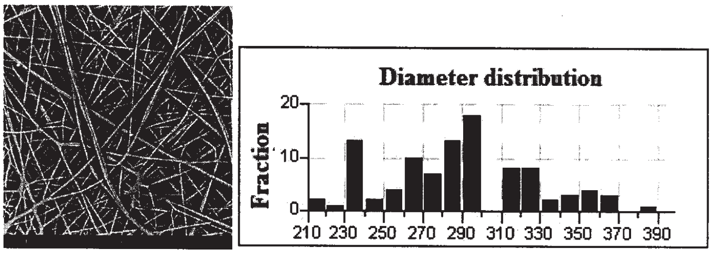
Electric field is a parameter that affects the morphology and diameter of nanofibers. It has been observed a decrease in the diameter of electrospun nanofiber with increasing the applied voltage. In order to clarify the effect of the electric field force, were conducted a series of experiments of electrospun polyvinyl alcohol solutions at different applied voltages from 14 kV to 40 kV. When the electric field is increased and the distance between the rod and the electrode collector is constant, an effective force that pulls and elongates the jet increases too. As a result, fiber diameter decreases. In addition, the diameter of the fiber is also obtained by combining the effects of flow rate of the jet and electrostatic force due to the applied voltage [36-40].

Figure 6 shows SEM images of 14% wt PVA electrospun nanofibers under different applied voltages (18.5 kV, 19 kV, 20 kV, 26 kV and 30 kV, respectively), while other conditions are kept constant (distance from the rod electrode (d) = 7 cm, atmospheric humidity (RH) = 44%, temperature (T) = 14.4 °C). It is observed that, for a 14% wt PVA polymeric solution, under the influence of certain applied voltages, fibers diameter changes from 255,46 nm to 206,39 nm. In addition, if the applied voltage is higher, nanofibers have a uniform morphology, but a high density of droplets on their surface.



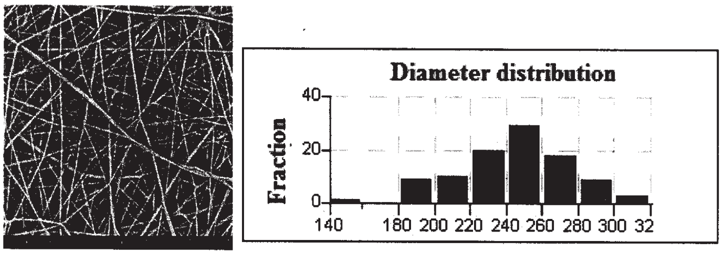

A.

14% wt PVA, d=7 cm, RH=44%, T=14,4 °C, 18 kV, average diameter = 255,46 nm



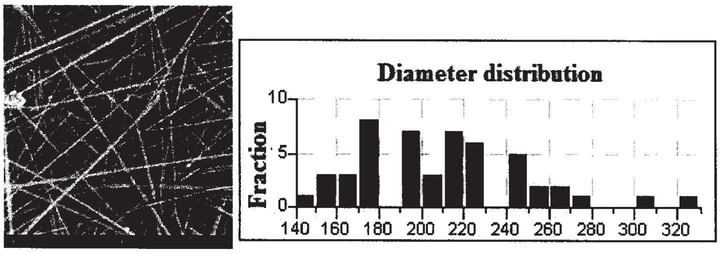

B.

14% wt PVA, d=7 cm, RH=44%, T=14,4 °C, 19 kV, average diameter = 248,07 nm




C.

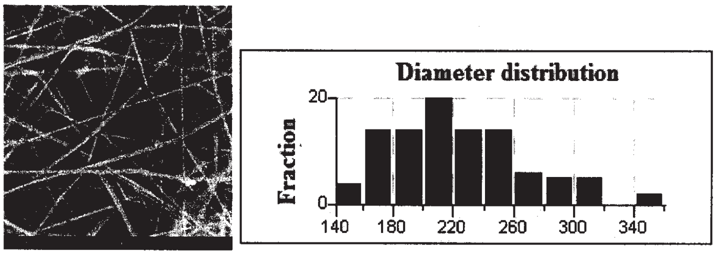
14% wtPVA, d=7 cm, RH=44%, T=14,4 °C, 20 kV, average diameter = 227,02 nm




D.

14% wt PVA, d=7 cm, RH=44%, T=14,4 °C, 26 kV, average diameter = 209,41 nm

Fig. 6A-D. SEM images of electrospun nanofibers 14% wt PVA under different applied voltages




E.

14% wt PVA, d=7 cm, RH=44%, T=14,4 °C, 30 kV, average diameter = 206,39 nm

Fig. 6E. SEM images of electrospun nanofibers 14% wt PVA under different applied voltages

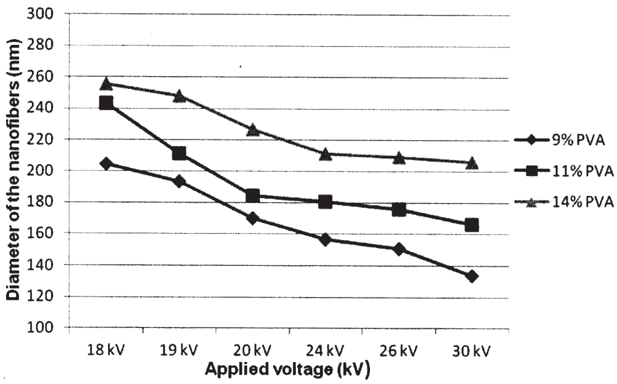



Fig. 7. The influence of the applied voltage on the diameters of the electrospun nanofibers

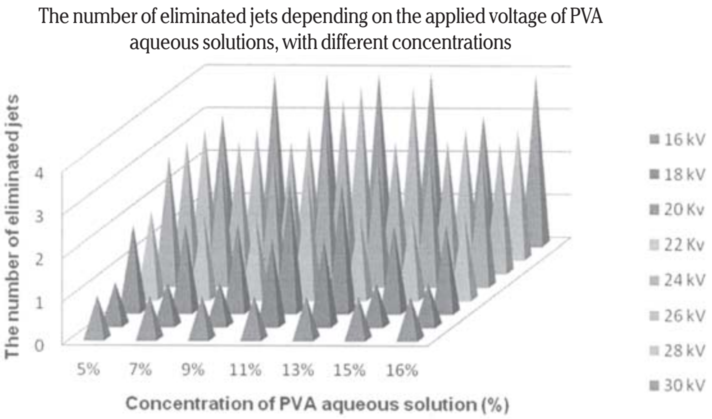



Fig. 8. Number of eliminated jets from a droplet of PVA polymeric solution having different concentrations (5% wt, 7% wt, 9% wt, 11% wt, 13% wt, 15% wt and 16% wt PVA, respectively)

Figure 7 states the fact that the diameter of the electrospun nanofiber decreases with increasing of the applied electric tension. It uses 3 different concentrations of the PVA polymeric solutions, 9% wt PVA, 11% wt PVA, 14% wt PVA, respectively. Working conditions during the experiments are: the distance from the rod to the collector is 7 cm, atmospheric humidity (RH) is 44% and the temperature is 19.4 °C.

Figure 8 shows the number of eliminated jets from a droplet of PVA aqueous solution, depending on the concentration, temperature and humidity of the solution. The number of eliminated jets increases gradually with increasing of the applied voltage.

An interesting approach is represented by the influence of the applied voltage to the relaxation time of the polymer and the number of eliminated jets during electrospinning process (fig. 9). It is noted that, at a certain selected concentration, relaxation time of the polymer decreases as the applied voltage increases, and as the concentration increases, relaxation time of the polymer increases too.

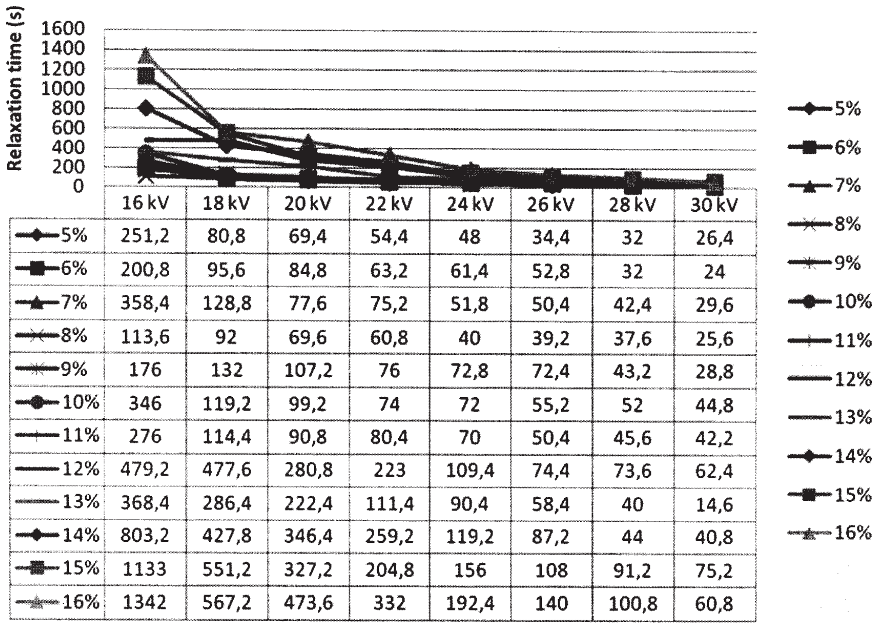
*The effect of the concentration of polyvinyl alcohol aqueous solutions*

It is well known from the literature that the concentration of the polymer is one of the most important parameters in the electrospinning process, having a significant effect on the final size of the nanofibers, morphology of electrospun nanofibers being dependent on the viscosity of the solution [41-45].

The concentration of the polymeric solution influences forming and density of the droplets, morphology and diameter of electrospun nanofibers. As shown in figure 11, the droplets dissapear with increasing concentration. Solution viscosity, charge density and surface tension are the main factors to form droplets [1-3]. Solution viscosity, at low concentration, is relatively lower than the surface tension. Generally, if the charge density is higher and the surface tension is lower, the formation of droplets is eliminated. In table 3 are given the values of the surface tension for PVA polymeric solutions with concentrations between 5% wt-16% wt and the resulted products from electrospinning of these solutions and the relationship between solution concentration and surface tension is shown in figure 10. Can be observed that with increasing polymeric solution concentration, surface tension increases too and the presence of droplets is also becoming smaller.

In order to confirm the above results, in experiments were used 12 polymeric concentrations in the 5% wt-16% wt range. SEM images of obtained PVA nanofibers, with concentrations in the range indicated, are shown in figure 11.

The droplets are also the product of jet instability under electric field. When the concentration of the polymer is




| | 16 kV | 18 kV | 20 kV | 22 kV | 24 kV | 26 kV | 28 kV | 30 kV |
|---|---|---|---|---|---|---|---|---|
| 5% | 251,2 | 80,8 | 69,4 | 54,4 | 48 | 34,4 | 32 | 26,4 |
| 6% | 200,8 | 95,6 | 84,8 | 63,2 | 61,4 | 52,8 | 32 | 24 |
| 7% | 358,4 | 128,8 | 77,6 | 75,2 | 51,8 | 50,4 | 42,4 | 29,6 |
| 8% | 113,6 | 92 | 69,6 | 60,8 | 40 | 39,2 | 37,6 | 25,6 |
| 9% | 176 | 132 | 107,2 | 76 | 72,8 | 72,4 | 43,2 | 28,8 |
| 10% | 346 | 119,2 | 99,2 | 74 | 72 | 55,2 | 52 | 44,8 |
| 11% | 276 | 114,4 | 90,8 | 80,4 | 70 | 50,4 | 45,6 | 42,2 |
| 12% | 479,2 | 477,6 | 280,8 | 223 | 109,4 | 74,4 | 73,6 | 62,4 |
| 13% | 368,4 | 286,4 | 222,4 | 111,4 | 90,4 | 58,4 | 40 | 14,6 |
| 14% | 803,2 | 427,8 | 346,4 | 259,2 | 119,2 | 87,2 | 44 | 40,8 |
| 15% | 1133 | 551,2 | 327,2 | 204,8 | 156 | 108 | 91,2 | 75,2 |
| 16% | 1342 | 567,2 | 473,6 | 332 | 192,4 | 140 | 100,8 | 60,8 |

Fig. 9. The influence of the applied voltage on the relaxation time of the polymer

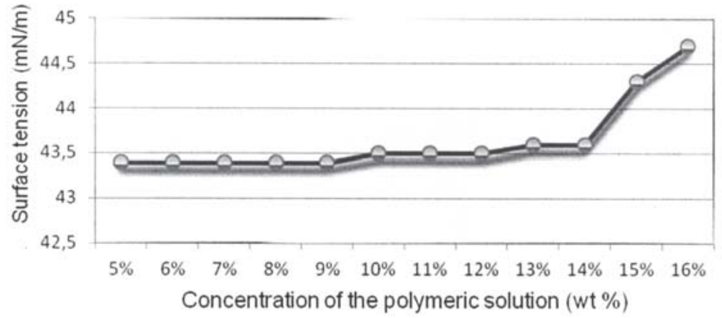



Fig. 10. The relation between the concentration of the polymeric solution and the surface tension

**Table 3**
THE INFLUENCE OF DIFFERENT CONCENTRATIONS OF PVA POLYMERIC SOLUTIONS AND SURFACE TENSION ON THE MORPHOLOGY OF THE OBTAINED NANOFIBERS

| Concentration of the polymeric solution (%) | Surface tension (mN $m^{-1}$) | Electrospun products |
|---|---|---|
| 9 % | 43,4 | Nanofibers with a high density of beads |
| 11 % | 43,5 | Nanofibers with a low density of beads |
| 13 % | 43,6 | Nanofibers with a low density of beads |
| 15 % | 44,3 | Nanofibers with a few beads |
| 16 % | 44,7 | Nanofibers |

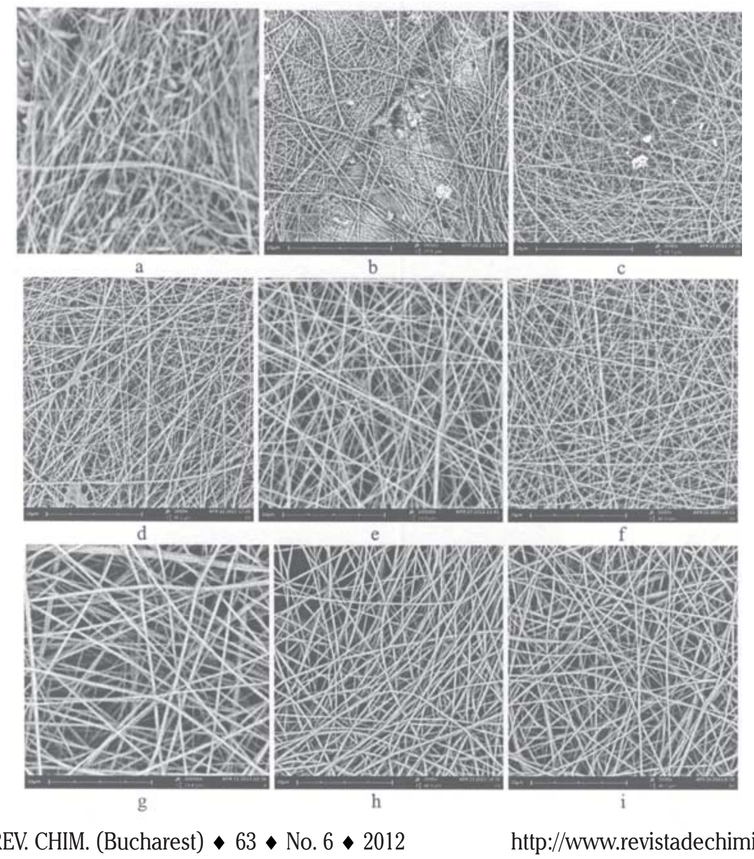



Fig. 11. SEM images of the PVA nanofibers as a function of solution concentration (voltage: 24 kV; distance between electrode-collector: 10 cm): a) 5 wt% PVA, d = 10 cm, RH = 44%, T = 20.7°C, 24 kV; b) 9% wt PVA, d = 10 cm, RH = 38%, T = 20.7°C, 24 kV; c) 10% wt PVA, d = 10 cm, RH = 50%, T = 19.4°C, 24 kV; d) 11% wt PVA, d = 10 cm, RH = 44%, T = 20.7°C, 24 kV; e) 12% wtPVA, d = 10 cm, RH = 51%, T = 19.3°C, 24 kV; f) 13% wt PVA, d = 10 cm, RH = 35%, T = 18.4°C, 24 kV; g) 14 wt % PVA, d = 10 cm, RH = 43%, T = 20.7°C, 24 kV; h) 15% wt PVA, d = 10 cm, RH = 35%, T = 20.7°C, 24 kV; i) 16% wt PVA, d = 10 cm, RH = 35%, T = 20.7°C, 24 kV

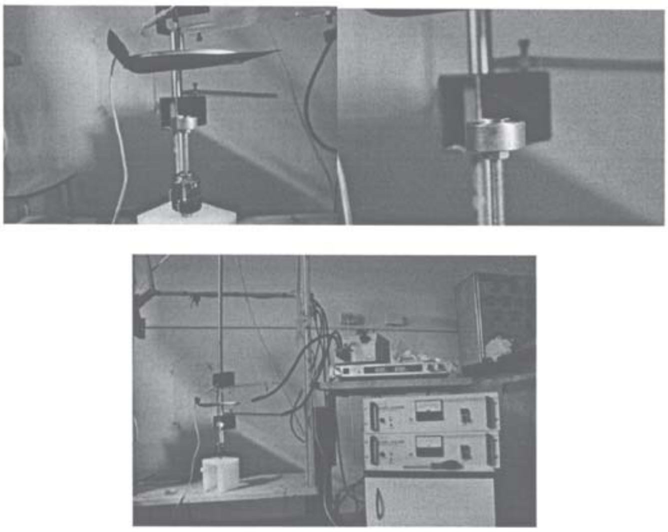


Fig. 12. The collector used in electrospinning process for a 2% wt PVA aqueous solution

low, the electrospinning process generates a mixture of fibers and droplets, and the process becomes an electrospraying process when the concentration becomes quite low. Increasing the concentration of polymeric solution, therefore, may decrease the number and size of the droplets, removing them completely in some cases and also increases the diameter of PVA nanofibers.

At a concentration of 5% wt PVA, nanofibers have on their surface a high density of droplets. As the concentration of the solution increases, the droplets gradually changes from spherical to spindle-like shape and if the concentration increased, the droplets gradually disappear. The number of droplets gradually decreases with increasing the concentration of polymeric solution from 5 wt to 16% wt PVA. Only a few drops can be observed on the electrospun fibers with 11% wt PVA concentration, while smooth, continuous fibers, with a larger diameter are obtained at a 14% wt PVA concentration. Therefore, there are no droplets and microspheres in electrospun products when the concentration of the polymer reaches 16% wt PVA and the resulted fibers are more uniform. The reason for this may be that the droplets are mainly caused by surface tension which minimizes surface area. If there isn‘t surface tension, the jet will be broken into droplets. A low surface tension tends to form several droplets in the electrospun products. With increasing of the polymeric solution concentration, surface tension becomes increasingly larger, resulting in fewer droplets.

If the concentration of the PVA polymeric solution is too small, the electrospraying phenomenon appears (St. Elmo fire - as it is called in the scientific literature). This phenomenon takes place between two electrodes with small radii. One of the electrodes has small dimensions and is generator of intense field. The other electrode has a larger radius and a flat surface. Discharging is positive, depending on the polarity of the small dimensions electrode. Corona discharge can be better observed in a dark room.

When the concentration of polymeric solution has values less than 5% wt PVA, the collector surface forms droplets instead of nanofibers. The light from these corona discharges becomes more intense when the applied voltage increases. The collector used (fig. 12) has a circular section, with a small inner section, on which polymeric solution is fed. The applied voltage reaches the value of 40 kV, the distance from electrode to collector is 7 cm, atmospheric humidity is 49% and temperature is 21°C.

## Conclusions

On the basis of studies regarding obtaining of polymeric nanofibers from electrospinning of polyvinyl alcohol aqueous solution, using an electrospinning device equipped with a rod electrode with a diameter of 8 mm and a lenght of 170 mm, reffering to the two groups of characteristics that influence the structure and morphology of nanofibers, following conclusions can be drawn:

- voltage or current is one of the most important parameters of needleless electrospinning, with direct influence on the structure and morphology of nanofibers, acting on the flow dynamics of aqueous polymeric solution. The applied voltage to the rod spinning electrode was between 0-40 kV, domain in which the influence on the elongation level of the jet can be felt, with a direct action on the surface morphology of the nanofibers and on the relaxation time of the polymer, respectively. The number of jets increases gradually with increasing of applied voltage, while the polymer relaxation time decreases. Also, increasing of the applied voltage lead to increasing deposition rate by increasing the amount of electrospinning mass, favoring the obtaining of nanofibers with a uniform morphology and high density of droplets on their surfaces. Instead, the lenght and diameter of nanofibers decreased with increasing of the applied voltage;
- concentration of aqueous polyvinyl alcohol solutions causes a certain viscosity that influences directly proportional the diameter and surface morphology of electrospun nanofibers. It was found that using small concentrations (5% wt), whatever the applied voltage is, the polyvinyl alcohol aqueous solution forms droplets instead of nanofibers and the electrospraying process appears. Increasing the concentration causes a fusion of droplets in nanofibers, because droplets modified from spherical to spindle-like form and the distance between the droplets increases with increasing viscosity, uniform nanofibers with larger diameters can be obtained. The range of concentrations where can be obtained uniform nanofibers, without droplets, is between 10% wt and 16% wt polyvinyl alcohol in water and the uniformity of electrospun nanofibers increases with the increase of polymeric solution concentration in this area.

The data obtained allows opening of new directions of research in this area both in terms of the influence of parameters which contribute to the design and modelling of surface morphology of technology obtained by needleless electrospinning technology with a rod, and in terms of the influence of some additives on the type of surface active agents or surfactantes, which are the subject of the next note.

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