INNOVATING TECHNOLOGIES FOR NANOFIBERS ACHIEVEMENT THROUGH ELECTROSPINNING SYSTEM

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Abstract: The present paper develop a technology for nano-fiber production by means of a computer controlled electrospinning system developed based on the idea of modularity and computerized control. Nanofibers achievement through electrospinning computerized system is innovative by specific technologies software and by the features of computerized control equipment which allow us to command and control the following parameters: high voltage in two ways: at constant tension and constant current, the flow of polymer solution, the control volume of polymer solution into the syringe, in use, the speed of the nozzle, wide nozzle movement, speed of rotation of the collector, for a cylindrical collector, speed of movement of the collector, for other types of collectors, the temperature of the air, the humidity of the air, the air speed that process occurs, the distance between the nozzle and the collector, the value of electric current that flows through the nanofiber, the electric field distribution along the nanofibre, speed nozzle cleaning needle tip in the operation.
Key words: technology, electrospinning parameters, nanofiber, system, process.

1. INTRODUCTION

Electrospinning is one of the most important techniques to manufacture nano-fibers. The theory is based on the electrostatic force that acts on the polymer solution. When introduced into the electric field, the solution will suffer from the electrostatic force, will accelerate, undergo jet instability and split into nano-fibers. At present, more that 100 different polymers have been electrospun into ultra fine fibers, with diameters ranging between 40–2,000 nm. In spite of the surging interest in electrospinning, research focuses on the structure and morphology of the fibers.

The technology for obtaining nanofibers originates in the work ”De magnete, magneticisque et de magno magnete tellure” in which William Gilbert describes the magnetic and electrostatic phenomenology of the electrospinning process. Formhals accomplished the first patent concerning the obtaining of the nanofibers by the electrospinning processing (Formhals, 1934). Taylor studied the mathematical modelling of the behavior of the Newtonian viscoelastic polymer jet electrically charged generated during the electrospinning processing (the shape of the cone formed by a fluid drop under the effect of an electric field); this shape of the drop is usually called the Taylor cone. Many researchers have studied throughout the years the effect of the various parameters (technological, constructive and environmental ones) upon the structure and characteristics of the electrospun nanofibers, for instance, the dependence of the fiber diameter upon the viscosity of the electrospun polymeric solution (Baumgarten, 1934), the influence of the electric field and of the environmental parameters upon the stability/instability of the electrospun polymeric jet (Hayati et.al., 1987), the instability of the polymeric jet processing and the factors influencing it (Reneker & Fong, 2001). After 1997 more and more researchers have thoroughly studied the electrospinning process although only a few papers have been published before 2000.

The technology employed for our electrospinning installation leads to the following advantages: both the technology and the specific software technology allow the computer equipment to conveniently obtain high quality, exceptionally long nanofibers, including nanotubes and mesh generation for medical applications; the various media filtering system allows the adaptation of technology for various polymer solutions.

2. ELECTROSPINNING TECHNOLOGY

In the electrospinning process (Fig. 1) we use a high voltage source to create an electrically charged jet of polymer solution. An electrode connected to the high voltage unit is immerged into the polymer solution contained within a capillary tube. The other one is connected with the collector at a distance of about 20 cm from the capillary tube. The solution is held by the surface tension in the form of a droplet when no power is supplied. The electric field is applied to an end by the capillary polymer containing fluid. This induces a charge on the liquid surface. Mutual rejection of the charges acts as a force directly opposite the surface tension. As the voltage is increased, the droplet will be elongated; when the supplied voltage reaches a certain voltage, a single solution jet will eject from the apex of a conical droplet (Taylor, 1969). The increasing electric field reaches a critical value for rejection when the electrostatic force exceeds the surface tension and when an electrically charged jet of fluid is injected from the tip of the Taylor cone. Injected polymer solution jet begins a process of turning in which the solvent evaporates leaving behind a polymer fiber with electrical charge and is placed randomly on a grounded collecting metal screen.

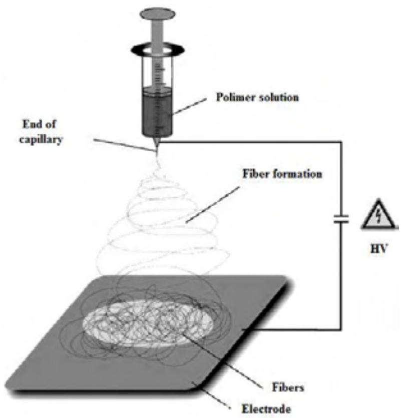


Fig.1. The general basic diagram of the electrospinning process

Before precipitating, the solution jet will undergo jet instability (about several centimeters away from the capillary) and it will split into small filaments collected on the collector in the form of non-woven fibers (Cramariuc et al., 2009).

The jet instability is due both to the perturbations of the surface charge and to the repulsive force of the jet current. The jet instability in electrospinning includes: axisymmetric instability and bending instability. The jet instability plays an important role in the formation of nanofibers. In the process of the jet instability, the solution jet suffers from constant shear flow, it elongates and splits into smaller filaments. Thus, the way to increase the jet instability stands at the basis of obtaining nanofibers. In polymer solution, the flexible molecule orients easily and the jet instability is fierce, so fibers with smaller diameters will be obtained.

A series of parameters act synergergically during the electrospinning process. The structure and the properties of the nanofibers are correlated with the usage domain, a fact that imposes a proper correlation of all these parameters of the electrospinning process.

The determination of the nanofibers characteristics involves knowing in advance the following features related to the solution processed polymer: molecular weight, molecular weight distribution, viscosity, conductivity, dielectric constant of the solution, surface tension, density polymer solution. Besides the parameters which belong to the polymer solution, one should also take into account the polymers belonging to the system and process, namely, the electric potential, the flow rate, the concentration, the distance between the capillary and the collector screen, the movement of the target screen, the environmental parameters (temperature, humidity and air speed in the room).

By modifying the single spinneret design, different electrospinning speeds can be obtained and different properties can be introduced into nanofibers. The modifying of the single spinneret with a number of channels/capillaries leads to the bi-component and triple or multi-component electrospinning. For bi-component electrospinning, the controlling of the location of the two channels/capillaries with coaxial and side-by-side ways resulted in coaxial and side-by-side electrospun fibers. Moreover, coaxial electrospinning becomes gas-jacketed/assisted electrospinning after replacing one polymer solution by gas in the outer tube. Also multi-jet and needle-less electrospinning are designed for the mass production of the electrospun nanofibers.

3. MATERIALS AND METHODS

3.1 Materials

To validate the electrospinning technology on the computerized electrospinning system, a technology based on our own experiments, the polyethylene oxide (PEO) with a gram-molecular weight of 300,000 (g/mol) (Aldrich) has been used; 99% chloroform and water-combined ethanol have been employed as solvents. The solutions were prepared at room temperature and gently stirred to speed dissolution. In the case of the PEO+chloroform solution one can notice that the dissolution has been done during a longer time period (12 hours) while in the case of the ethanol the dissolution has been done much faster (Fig. 3).


a b

Fig. 2. 3% PEO/chloroform solution: a. sample taken immediately after the stirring of the polymer with the solvent; b. sample taken at 6 hours after dissolution

Fig. 3. Aspect of the PEO solution in the moment when the polymer has been added

3.2 Experimental Part

The PEO solutions in chloroform and ethanol/water have been electrospun. The PEO concentrations have ranged between 2–6 wt%.

The prepared solutions have been experimented on the computerized electrospinning system. A 3 ml syringe with a 10 mm diameter and an inner diameter of the needle ranging from 0.7 and 0.8 mm has been used. The needle has been connected to a high-voltage source generating a positive voltage up to 30 kv. To collect the nanofibers we have used two types of collectors, namely, a metallic rotary drum with a rotary speed of 500 rev/min, and a plane surface one connected to a feeding source.

The distance between the capillary and the collector has been progressively varied between 45 – 110 mm. The solution flow rates have been controlled by a syringe pump and ranged from 0.5 to 8 ml/h. All electrospinnings have been carried out at room temperature.

4. RESULTS AND DISCUSSION

In the case of the experiments accomplished with a PEO/chloroform solution with a feeding rate of 6 ml/h both the distance between the capillary and the collector as well as the applied voltage have been varied. As a result of these experiments and from the view point of the characteristics of the obtained fibers, we have considered as an optimum variant the processing carried out at a 10kV voltage and a distance between the needle and the collector of 50 mm. The obtained fibers are shown in Fig. 4.

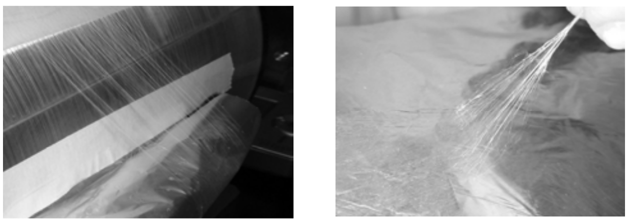


Fig. 4. Image presenting PEO/chloroform nanofibers when detaching from the rotary drum

In the case of the experiments accomplished with a PEO/ethanol solution, the optimum results from the view point of the fibers characteristics have been obtained at a feeding rate of 1 ml/h, at a 15kV voltage and a distance between the needle and the collector ranging from 45 mm to 100 mm. The obtained fibers are shown in Figs. 5, 6 and 7.

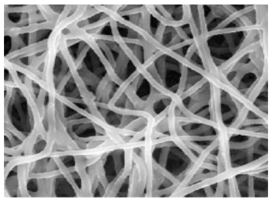


Fig. 5. SEM image of the PEO/chloroform nanofibers

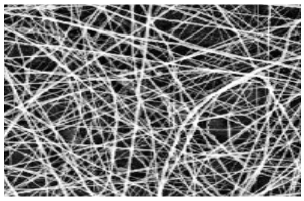


Fig. 6. SEM image of the PEO/ethanol nanofibers

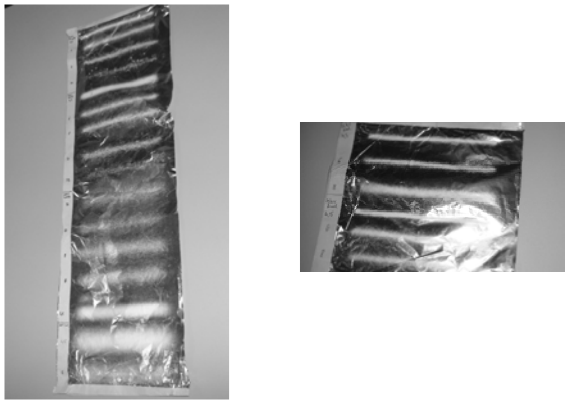


Fig. 7. Nanofibers deposited on the aluminium foil taken from the plane collector

From the experiments carried out by employing the other value sets of the varied parameters there have been obtained either drop fibers or only drops, a fact depending on the applied voltage, solution feeding rate as well as on the distance between the capillary and the collector (Figs. 8 and 9). Other phenomena which have appeared during the electrospinning processing are the following: curling and bending instabilities of the jet which determine the magnitude of the spraying ratio and a great deposition surface of the fibers or the appearance of the splitting phenomenon of the jet and, respectively, the obtaining of short fibers due to the too high conductivity of the polymeric solution processed by electrospinning.

The formation of beads and beaded fibers is driven by the surface tension. Surface tension tries to make the surface area per unit mass smaller, by changing the jets into spheres. The forces from the excess charge try to increase the surface area, which opposes the formation of beads and leads to thinner jets. The major competition is between the surface tension and the viscoelastic force. The increase of the viscosity favors the formation of smooth fibers. Another competition is between the electrical force and the viscoelastic force. The increase of the net charge density and the associated electrical forces favors the formation of smooth fibers. The bead diameter and the spacing are related to the fiber diameter: the thinner the fiber is, the shorter the distance between the beads and the smaller the diameter of the beads are.

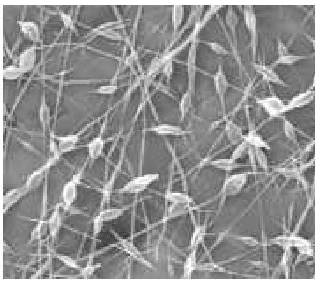


Fig. 8. Fibers with beads from PEO/chloroform solution electrospinning

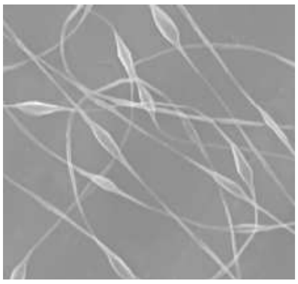


Fig. 9. Fibers with beads from PEO/ethanol solution electrospinning

In the case of the PEO/chloroform solution electrospinning, the process has been stable only when the feeding rate has been maintained at a minimum value of 1 ml/h. Below this value, the rapid solidification of the polymers at the needle tip has blocked the solution inside the needle. The voltage has been found to be a critical parameter in the production of non-beaded fibers. At 8 kv, the fibers have presented many beads even if the electrospinning process has been perfectly stable. By increasing the voltage, the beads have progressively disappeared from the fibers and non-beaded fibers have been obtained above 15 kV.

The viscosity of the solution decisively influences the fiability by electrospinning both of the processed polymeric solution and of the morphology of the resulted fibers. As a result of our experiments, one can estimate that the solution viscosity depends on the complexity degree of the molecular chains of the processed polymer. At reduced viscosities when, generally speaking, the complexity of the polymer chain is reduced, there exists an increased probability to obtain fibers with ”beads” instead of the smooth ones. Thus, the factors which affect the viscosity of the solution will also affect the electrospinning process and the characteristics of the resulted fibers.

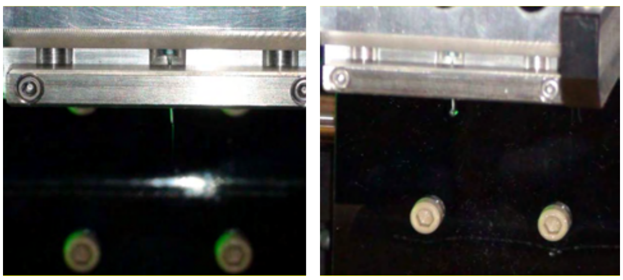
The characteristics of the processed polymeric solution plays a significant role in the processing method (electrospinning) and influence the characteristics and the morphology of the fibers. During the electrospinning process the polymer solution is drawn from the tip of the syringe; the electric properties of the polymeric solution as well as the surface tension and the viscosity, respectively, will determine the spreading degree of the solution. The solubility of the polymer in the solvent is another important characteristic with significant influences upon the solution viscosity.

For the fibers delivery through the electrospinning process to take place, the solution must acquire sufficient electric charge so that the repulsion forces from the solution should exceed the surface tension of the solution. The elongation of the electrospun jet (the subsequent drawing) also depends on the capacity of the solution to convey electric charges.

Generally speaking, the electric conductivity of the solvents is very low (usually between 10^{-3} and 10^{-9} ohm^{-1} m^{-1}) because they hardly contain free ions which are responsible for the electric conductivity of the solution. The presence of the acids, bases, salts and of the dissolved carbon dioxide can increase the conductivity of the solvent. The electric conductivity of the solvent can be significantly increased by mixing the compounds which do not produce chemical reactions. Among the substances which can be added to increase the conductivity one can mention mineral salts, mineral acids, carboxylic acids, some complexes of amino-acids, tin chloride, certain tetra-alkyl-ammonic salts. In the case of the organic acid solvents, the addition of a small quantity of water will significantly increase the conductivity due to the ionization of the solvent molecules.

4.1. Influence of the technological parameters upon the characteristics of the electrospinning-obtained nanofibers

The influence of the technological parameters upon the characteristics of the electrospinning-obtained nanofibers has been studied for the 6% PEO/ethanol and chloroform polymeric solution. The adopted variation limits of the electrospinning parameters employed during our experiments with a view to obtain nanofibers by means of the ELECTROSPIN equipment are the following: 10-15 kV applied voltage, 50-120 mm needle – collector distance, 1-4 ml/h feeding speed (Q). During our experiments on the ELECTROSPIN equipment the following parameters have been kept constant: Q=1ml/h feeding speed, V=10kV applied voltage, the needle – collector distance (d) being ranged between 45 and 120 cm. After experiments we have noticed that there have been obtained fibers at small working distances, i.e. 45 and 50 mm, respectively (Fig. 10a). At a 60 mm needle – collector distance there have been obtained drop fibers while for the values of 80 or 100 mm needle – collector distances there have been obtained drops due to the decreasing of the electrical field at the same time with the increase of the needle – collector distance (Fig. 10b).



a. b.

Fig. 10. Electrospinning delivery

a. Continuous jet (Q=1ml/h, V=10kV, d=60cm, syringe diameter=10 mm, syringe volume= 3 ml, needle inner diameter=0.7 mm); b. Polymeric solution drop formed at the needle tip (Q=1ml/h, V=10kV, d=100cm, syringe diameter=10 mm, syringe volume= 3 ml, needle inner diameter=0.7 mm)

At small needle – collector distances the delivered fibrous depositions have presented faults and, respectively, the nanofibers have been stucked together, a phenomenon due to the reduced evaporation time under the condition of the small needle – collector distances. At the same time with the increase of the needle – collector distance, the evaporation time also increases, and, implicitly, dry fibers with good uniformity are obtained. This thing can be explained by the fact that the mass equilibrium which appears between the polymeric solution and its moving away from the needle has not been kept under a too small or too great applied voltage (Fig. 11).

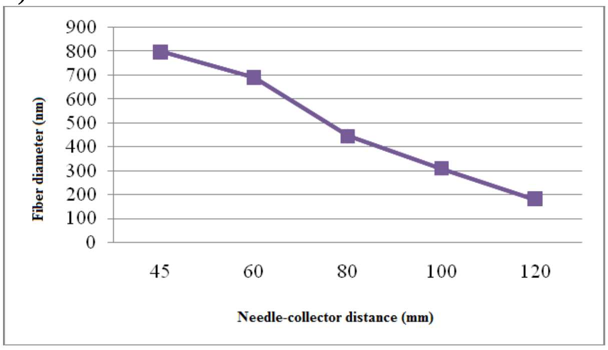
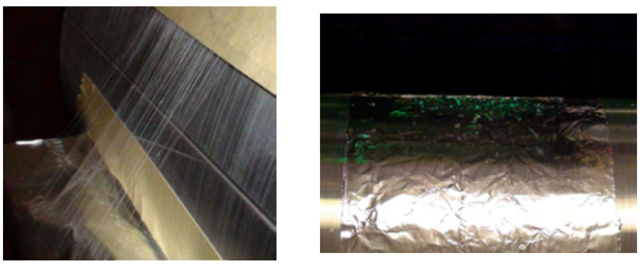


Fig. 11. Influence of the needle – collector distance upon the fiber diameter (Q=1ml/h, V=10kV, d_1=45cm, d_2=60cm, d_3=80cm, d_4=100cm, d_5=120cm, syringe diameter=10 mm, syringe volume= 3 ml, needle inner diameter=0.7 mm)

The experiments have rendered evident the fact that at the same time with the increase of the needle – collector distance fibers with a better uniformity are obtained, but the exceeding of a certain optimal level, technologically determined upon the correlation of the other constructive and technological parameters, leads to the obtaining of fault fibers. During the electrospinning process there have been kept constant the following technological parameters: feeding speed (Q=1 ml/h), needle – collector distance (d=45 mm), the applied voltage (V) varying between 10 and 15 kV. Fibers have been obtained for all three values of the voltage (Fig. 12a). In the case when Q=1 ml/h and d=120 mm have been kept constant and the voltage has been varied from 10, 12, 15 kV, fibers with drops and drops have been obtained (Fig. 12b).



a b

Fig. 12. a. Fibers detached from the collector; b. Drops deposited on the collector (Q=1ml/h, V=10kV, d=60cm, syringe diameter=10 mm, syringe volume= 3 ml, needle inner diameter=0,7 mm)

The PEO fibers obtained at the smallest voltage, i. e. 10kV, have shown an uniform morphology. At higher voltages, the uniform morphology has been kept but more drops have appeared on the collector surface. Therefore, we can state that the applied voltage is correlated with the drops formation due to the effect it has upon the shape of the drop at the needle tip. We have also noticed that at the same time with the increase of the applied voltage there appears a small decrease in the fibers diameter due to a better stretching of the polymeric solution (of the jet) (Fig.13).

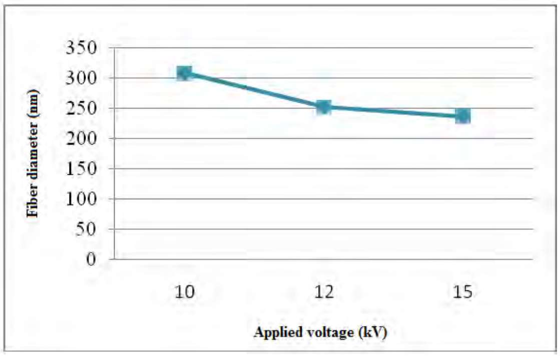
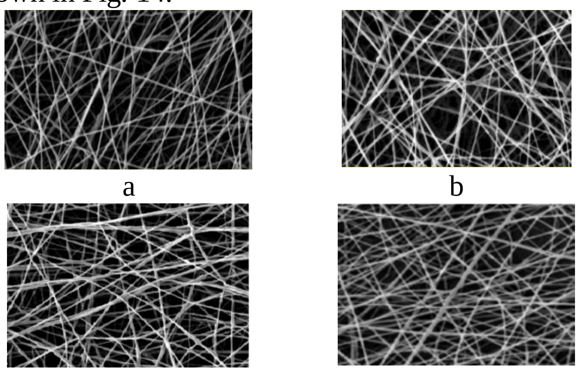


Fig. 13. Influence of the applied voltage upon the fiber diameter (Q=1ml/h, V_1=10kV, V_2=12kV, V_3=15kV, d=60cm, syringe diameter=10 mm, syringe volume= 3 ml, needle inner diameter=0.7 mm)

SEM images for various technological parameters are shown in Fig. 14.



c d

Fig. 14. SEM images of the PEO electrospun nanofibers (a. Q=1ml/h, V=10kV, d=4.5 cm; b. Q=1ml/h, V=12kV, d=4.5 cm; c. Q=1ml/h, V=15kV, d=4.5 cm; d. Q=1ml/h, V=10kV, d=120 cm)

The accomplished experiments have rendered evident the fact that at the same time with the increase of the applied voltage there appear drop-type faults on the fibers surface.

During the electrospinning process there have been kept constant the following technological parameters: applied voltage (V=10kV), needle – collector distance (d=45 mm), the feeding speed (Q) varying between 1 and 4 ml/h. For the three values of the feeding speed there have been obtained short fibers as well as drop fibers, whipping instabilities being also noticed (Fig. 14b).

A greater diameter of the capillary allows a higher feeding rate which must be accompanied by the increase of the voltage and of the electrical field power (Fig. 15) and which leads to obtaining greater diameter fibers. There has been noticed that the diameter of the PEO electrospun fibers increases with the increase of the feeding rate, a thing understandable by the fact that there exists a greater quantity of solution available for electrospinning under the condition of a higher feeding rate. The experiments have rendered evident the fact that a higher feeding speed leads to obtaining greater diameter fibers (Scârlet et. all, 2011).

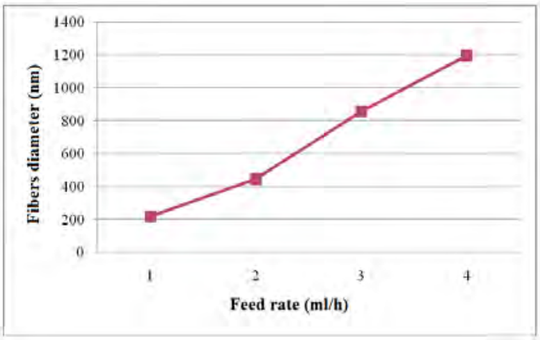


Fig. 15. Influence of the feeding rate on the fiber diameter (Q_1=1ml/h, Q_2=2ml/h, Q_3=3ml/h, Q_4=4ml/h, V=12kV, d=60cm, syringe diameter=10 mm, syringe volume= 3 ml, needle inner diameter=0.7 mm), [7]

The increase of the needle – collector distance leads to the diminishing of the formed electrical field but there is not possible the compensation of this decrease by increasing the voltage because the modification of the needle – collector distance leads to the change of the electrical field form. Thus, the distance determines the nature of the electrical field. A great needle – collector distance supports a more homogeneous electrical field which is advantageous from the view point of the uniformity of the deposited layers. A shorter distance leads to a ”bull eye”-type shape. The feeding speed of the polymeric solution is directly proportional with the productivity when the electrospinning process is at an optimal value and the whole solution leads to the formation of fibers, not drops. The feeding speed depends on the capacity of the capillary, the power of the electrical field, the solution viscosity, but it can also be determined by the type of the feeding mechanism. The forming speed of the fibers is also influenced by the power of the electrical field and by the solution viscosity, but also by some other parameters of the solution, for instance, conductivity. The main parameters which affect productivity are the strength of the electrical field, the needle – collector distance, the voltage. A greater diameter of the capillary allows a higher feeding rate which must be accompanied by the increase of the voltage and of the power of the electrical field.

5. CONCLUSIONS

Nanofibers achievement through the electrospinning computerized system is innovative by specific technologies software and by the characteristics of the computerized control equipment which allow us to operate and control the following parameters: high voltage in two ways: at constant tension and constant current, the flow of polymer solution, the control volume of polymer solution into the syringe, in use, the speed of the nozzle, wide nozzle movement, speed of rotation of the collector, for a cylindrical collector, speed of movement of the collector, for other types of collectors, the distance between the nozzle and the collector, the value of electric current that flows through the nanofiber, the electric field distribution along the nanofibre. Electrospun fibers are generally characterized by high surface area and small pore size, thus making the obtained materials excellent candidates for filtration and barrier applications, nanoelectronics, biomedical applications and optical devices.

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