Equipment for Obtaining Polimeric Nanofibres by Electrospinning Technology

II. The obtaining of polimeric nanofibers

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The computerized technologies and equipment for obtaining nanofibers impose high training, a large interdisciplinary substantiation, capacity for data storage, memorizing, easy usage, selectivity, fiability, stability, reduced time for analizing / processing of the technological parameters. That is why the computerized electrospinning equipment and technologies for obtaining nanofibers are possible candidates to carry out these requirements owing to the fact that they present both the proper selectivity / sensibility and the increased processing /determining /intervening speed by using the computerized control. This paper aims to present the operation and aplication of equipment for obtaining polimeric nanofibers by electrospinning technology. The designing and accomplishing of the suggested electrospinning equipment has been aimed to obtain a modular system which should allow the control of the technological parameters by means of the computer. Thus, the multitude of the parameters which influence the process of electrospinning, can be independently and automatically varied. The obtained nanofibers were studied by scanning electron microscope.

Keywords: nanofibers, equipment, technology, modular conception, electrospinning

The electrospinning technology involves the application of a very high voltage at one capillary and the polymer solution pumping through the nozzle by using a liquid pump. Nanofibers are collected as a nonwoven material on a grounded collector [1-9]. As a result of the applied voltage it is created a polymer solution jet (named also as melting jet) with a high electrical charge which will form nanofibers by solidification (fig.1).

One electrod is placed in the solution and another one is attached by a collector. The polymer fluid from nozzle end, kept by its superficial tension, is electrostatic charged; the mutual rejection of electric charges actions as an opposite force for superficial tension. By increasing the electric field intensity, the fluid hemispherical surface from the nozzle tip changes its length forming a cone named "Taylor cone". The continuation of the intensity increasing will reach a critical value when the electrostatic rejection force will be greater than superficial tension, and a fluid jet electrical charged will be ejected from the Taylor cone tip [10-13]. In the case of solution electrospinning, the polymer fluid jet begins a process of elongation and rotation so the solvent evaporates, leaving behind a polymer fiber electrically charged with nanoscale dimensions, which will reach randomly or in a linear way the grounded collector [14-17].

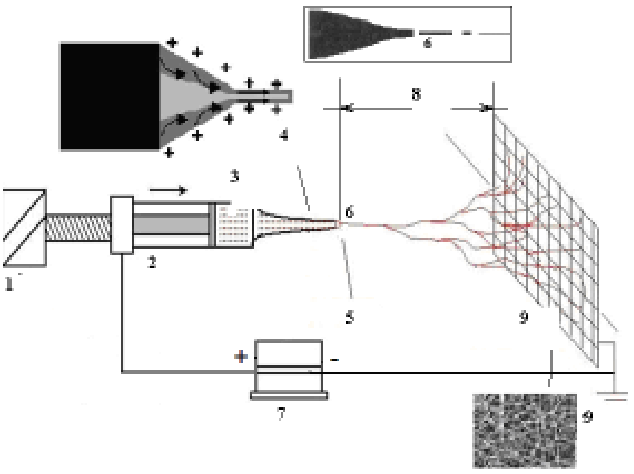

Fig. 1. Diagram of the electrospinning principle from polymeric solution: 1. proportioning pump; 2. syringe; 3. polymer solution; 4. pipette; 5. Taylor cone; 6. jet (photos of jet fragments at various distances from a capillary); 7. high-voltage source; 8. variable distance; 9. collecting screen, rotary or stationary

For a certain polymer solution, there are some levels of electric voltage and feeding speed for which the electrospin process can be maintained stable during long periods of time [2, 18-27]. Taking in consideration the jet

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disintegration mode into drops can be defined three types of instability (fig. 2):

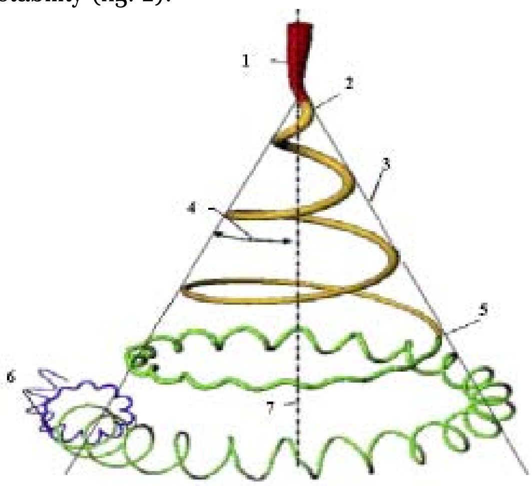


Fig. 2. The simulation of instability phenomenon [22]: 1. linear jet zone; 2. beginning zone of the first instability axial-symmetric; 3. jet trajectory left by the needle; 4. halving angle for trajectory cone; 5. the second zone of instability; 6. the third zone of instability; 7. jet axis

-axial-symmetric instability controlled by the superficial tension (non-conductor) or by the electrostatic forces (conductive) - it determines the drops formation;

- non-axial-symmetric instability (bending, conductive) depending on electrostatic forces; this type of instability is responsible for the process of jet elongation (thinning);

-„whipping" type instability that determines random spreading of jet and the fracture of jet into short fibers; this type of instability is allowed by the charge density increasing and polymer fluid rate flow.

A series of parameters act synergergically during the electrospinning process [1-3, 28-32]. The variables which influence, as decision factors, upon the morphological structure of the nanofibers are grouped, as shown in Table 1. Throughout the time there have been developed models which have anticipated the dimensional characteristics of the fiber for some solutions of polymer, at different concentration, depending on the surface stress and on the density of the volume load [33-48].

Experimental part

The operation of equipment for obtaining polimeric nanofibers

The constructive elements which accomplish the operation and control of the electrospinning equipment [49-

Table 1
FACTORS WHICH STRONGLY INFLUENCE THE STRUCTURE AND THE CHARACTERISTICS OF THE ELECTROSPINNING NANOFIBERS

Characteristics of the raw material	
• Type of polymer, form, content, viscosity, elasticity, electric conductivity of the polymer [S/cm], architecture/structure of the polymer (branched, linear); • Type of the solvent, volatility of the solvent (degree of evaporation of the solvent); • Molecular mass [g/mol], distribution/dispersion of the molecular mass, concentration [%] of the polymeric solution, transition temperature • Dielectrical constant of the polymer (polymer permittivity) $\varepsilon = \varepsilon_r \cdot \varepsilon_0$; • Electric moment of the dipole (1 Debye = $3{,}33564 \cdot 10^{-30}$cm; electric moment for 2 charges of 10^{-10} Franklin separated by 1 Ångström); • Free surface stress (surface pressure) [dyne/cm], (mN/m).	
Parameters of the equipment	
Technological parameters	Electric potential (electric field voltage) [kV];
	Flow rate (Q) [mL/min];
	Temperature gradients (melt electrospinning);
	Electrohydrodynamics of the evaporation and electrostatic charge;
	Total current of the jet [nA];
	Applied field E_∞ [kV/cm];
	Solid – liquid charge transfer;
	Displacement speed of the aim screen (collector) [m/s];
	Displacement speed of the nozzle [mm/s];
Constructive parameters	Distance between the capillary and the collecting screen (distance between the capillary nozzle to the collector), [mm];
	Contructive dimensions of the capillary, the tip of the capillary/the geometry of the drop $((\pi R_0\sigma)^{-1/2} < 4$, where R_0 is the radius of the equivalent volume of the drop, σ is the surface pressure coefficient), R_0 [cm];
	Syringe diameter, d [mm];
	Displacement range of the nozzle holder [mm];
	Constructive type of the collecting screen;
	Distance between the electrodes [cm].
	Number of nozzles;
	Distance between the nozzles [mm];
	Solution volume [mL];
Environmental parameters	
• Temperature of the environment in which the collecting of the nanofibers takes place, T [$^\circ$C]; • Atmospheric humidity, U[%]; • Ventilation in the environment [m^3/min]; • Vacuum permittivity, ε_0 [F/m] ; • Dry air permittivity, ε_{air} [F/m]; • Atmospheric pressure, P [atm].	

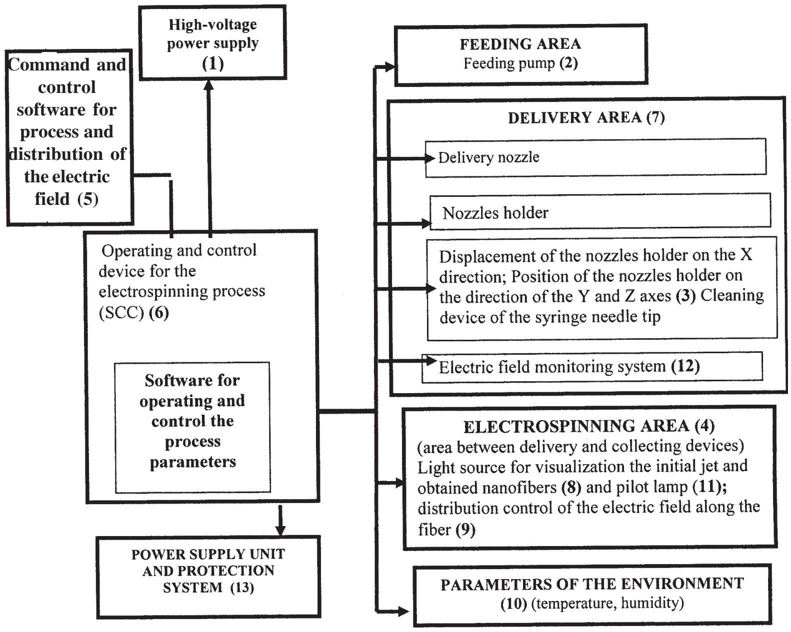


Fig. 3. Block diagram of the computerized electrospinning equipment

59] are shown in figure. 3. The entire equipment functioning described in figure 3 is based on general principles shown in figure 1 and 2. One pole of the high-voltage power supply (1) is connected to the nozzle that ejects the polymer fluid (7). The opposite pole is connected to the collector (4). Liquid pump (2) is linked to the nozzle (3). Power supply, liquid pump, the driving system for the nozzle (3) and for the collector (4) are connected to the computerized command system – SCC (6) which has dedicated software for command and control (5) of the entire process. Also there are connected to the computer: light source for visualization of initial jet and obtained nanofibers (8), device for distribution control of the electric field along the fiber (9), conditioning device for controlling the temperature and humidity (10), pilot lamp (11), monitoring system for the electric charge (12) and the power supply unit and protection system (13).

According to figure 3, power supply (1), polymer liquid pump (2), positioning system on Z axis for the nozzle (3), speed of the rotational collector (4), optical sensors from the light source (8), control device of the electric field distribution (9), conditioning system (10), monitoring system of the electric charge from electrospinning circuit (12), power supply unit and the protection system (13) are monitored and controlled by SCC (6) through the dedicated software (5). SCC consists of a computer and the necessary command devices for different electric drives (for example the nozzle and collector engine) and for data acquisition from sensors. The control of the parameters is done in real-time depending on the nanofibers properties (diameter, uniformity etc.). Information concerning nanofibers properties are extracted from automated computerized analysis of the interference and dispersion measured by perpendicular lighting of the fibers with a light source (8).

Power supply (1) from figure 3 is a DC supply type, digital, with numeric control. It is connected to SCC (6) that has dedicated software (5) which controls the voltage supplied by the source. The software adjusts in real-time the applied voltage during the entire electrospinning process depending on the properties of the obtained nanofibers. Liquid pump (2) is a digital one, numeric controlled by the software (5) which regulates the flow during the process depending on the properties of nanofibers.

The nozzle that ejects the polymer liquid (7) is placed on a driving system with computerized moving control on Z axis (3). This is realized by using a linear guiding device with a digitally regulator which is controlled by the software (5). The linear movement of nozzle along Z axis determines the distance between nozzle and collector – very important for nanofibers properties. The control software takes in consideration these properties and regulates the distance nozzle-collector in real-time. Cylindrical collector is actioned by a DC engine (4) having the speed numerical controlled by the software (5). This speed is correlated by the software with the speed of nanofibers production.

The conditioning system (10) is connected to SCC for recording and regulating the temperature and vapour saturation inside electrospinning equipment. Pilot lamp (11) is a uniform light system and an images acquisition device for visual observing of "Taylor cone" and the phenomenon of fiber producing. The intensity of pilot lamp is controlled by SCC (6). The electric charge monitoring system (12) has the role of observing the charge from electrospinning circuit nozzle-jet-collector-power supply and to transmit information to SCC. Supply unit (13) is connected to SCC which commands different electric actions to the component devices and data acquisition. For electric field controlling between nozzle and collector and for producing a stable jet/nanofiber, the equipment has an electric field distribution control device along the obtained nanofibers.

Another component of the field control device is an electromagnetic deflection module which has the role of nanofibers deviation on *X* direction, along the rotary collector drived by an engine and controlled by SCC. In this way it is possible to realize along the *X* direction a controlled nanofibers covering. The deflection module is fed by the high-voltage power supply. The electrostatic lens and the deflection module are individually controlled by SCC depending on the nanofibers properties.

The light device consists of laser light sources oriented perpendicular on fiber and an optical sensor connected to SCC. After the computerized processing of interference and dispersion measured from jet and nanofiber perpendicular lighting are obtained information related to diameter and uniformity during the entire process. This information are used as feedback mechanism for regulating technological and design parameters through applied voltage change by power sources, fluid pump flow, distance between nozzle and collector and rotary movement of the collector.

A high-speed digital camera with an optical system having a magnification in depth and large working distance is placed in pilot lamp direction for taking and transmiting processing images to SCC. These images are automated analyzed by SCC and they are part of control and monitoring mechanism of electrospinning process.

Testing the performances of the electrospinning equipment

Setting the working parameters for experiment

The processing stages for obtaining nanofibers are the following:

-the seringe feeding with polymer solution; the seringe is attached by the capillar through a transparent plastic tube (fig. 4);

-setting the feeding speed for polymer solution; this parameter may be chosen directly from the feeding pump display;

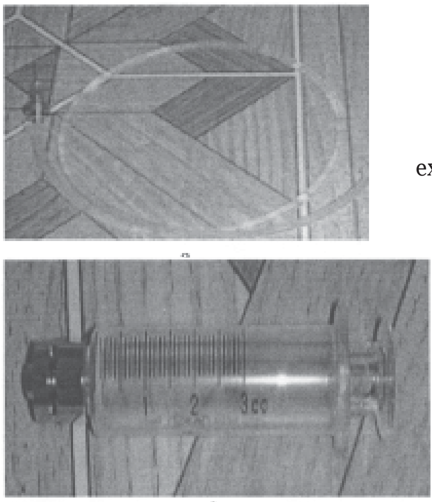
-setting the technological parameters: voltage, moving speed of the nozzle, rotary speed for the cylinder (tambour), spinning distance; these settings are done directly from the command and control unit of the equipment;

-also from the command and control unit it is set the nozzle moving interval along X axis;

-setting the design parameters: nozzle moving distance along the Z axis;

-setting the environental conditions: temperature and humidity.

There will be presented some parts of the experiments done for testing the performances of the electrospinning equipment.



b.

Fig. 4. Images from experiments: a. plastic tube connection.; b. Syringe

Preparation and Characterization of the Blend Solutions

Poly(ethylene) oxide (PEO) is a natural polymer, thus making it nontoxic, less likely to elicit an immune response. PEO with molecular weight of 400.000 g/mol was obtained from Aldrich. As solvent distilled water and ethanol was used. The ratio of the solvents was ethanol/water: 4/6. The solutions were mixed at room temperature with magnetic stirring for 24h (fig. 5).

The PEO concentrations have ranged between 2–6%. Only with four solutions had good results, with three concentrations: 3% - (P3), 4% - (P4), 5% - (P5) and 6% - (P6), with the other two solutions we were unable to electrospun.

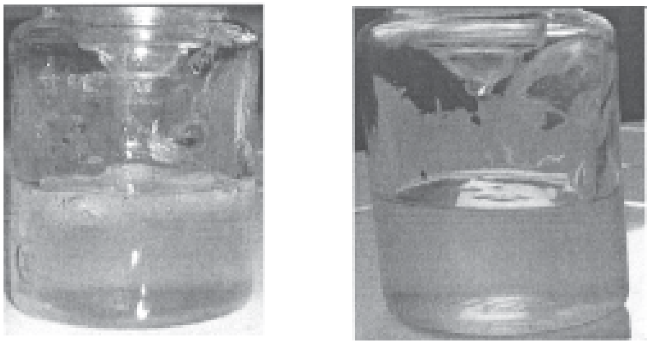


Fig. 5. Polymeric solution: a. at start; b. after 24 h

Properties and measurements

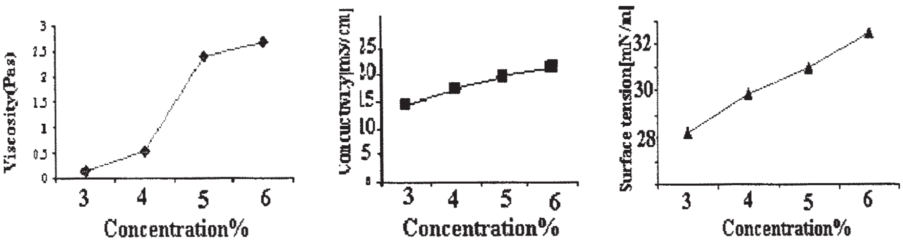
Before electrospinning, properties of the solutions have been measured such as surface tension, conductivity and rheological properties. Surface tensions of solutions were measured with Krüss apparatus using plate method. The conductivities of solutions were measured by conductivity meter Chromoservis 510 (Eutech Instruments). The rheological properties of solutions were measured with Gemini Rotational 2 using two functions of the apparatus: Viscometry (determine zero shear viscosity of solutions, behaviour of viscosity under shearing) and Oscillation (gives us value of complex modulus, viscous modulus, elastic modulus) [39-44, 49, 50].

Electrospinning

The prepared solutions have been experimented on the computerized electrospinning system. A 3mL syringe with a 10mm diameter and an inner diameter of the needle of 0.4mm has been used. The needle and the collector have been connected to a high-voltage source generating a positive voltage. To collect the nanofibers we have used a plane surface. All electrospinnings have been carried out at 25°C temperature and 35% humidity. The optimum parameters for all the solutions are presented in table 2.

The morphology of the electrospun nanofibers was observed with a Scanning Electron Microscope FEICO (Model Phenom G2 pro) manufactured by Phenom-World, Netherlands. The properties of nanofibers membrane as fiber diameter were determined by using Nis-Elements and Lucia software (fig. 7).

The experiments showed that the electric field intensity is not constant along the polymer jet axis, fact that explains the unevenness for the obtained deposits of fibers. The voltage increasing leads to electric field intensity increasing, but the shape of the field remains the same. In figure 8 can be seen the instabilities created by applied voltage (Q = 0.2mL/min, U = 15kV, d = 120mm, seringe diameter = 10mm, seringe volume = 3mL, needle interior diameter = 0.4mm).



a. b. c.

Fig. 6. Properties of PEO/water/ethanol solutions:
a. the viscosities of 3-6% PEO/water/ethanol solutions;
b. the conductivities of 3-6% PEO/water/ethanol solutions;
c. the surface tensions of 3-6% PEO/water/ethanol solutions

Sample	Concentrations (%)	Feeding rate (mL/min)	Voltage (kV)	Spinning distance (mm)	Average diameter (nm)
P3	3	0,2	15	70	285
P4	4	0.2	17	100	306
P5	5	0.2	30	100	391
P6	6	0.2	32	120	412

Table 2
THE OPTIMUM PROCESS PARAMETERS FOR THE SOLUTIONS

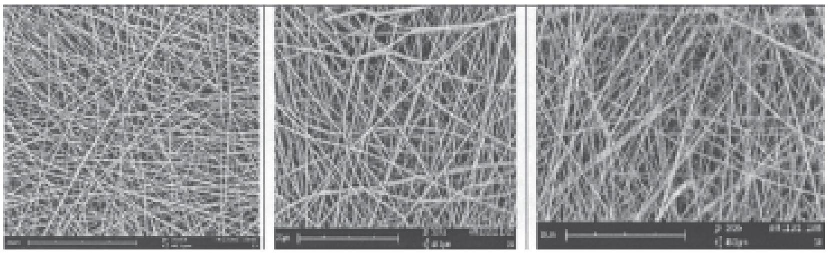


Fig. 7. The morphology of the electrospun nanofibers: a. 3%, b. 4% and c. 5% PEO/water/ ethanol solutions

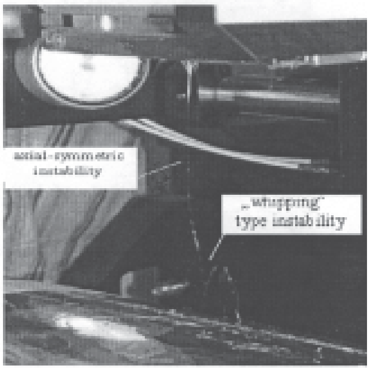


Fig. 8. The whipping type jet instability

After the experiments, there can be formulated a few conclusions concerning the prelucrability of PEO/ethanoL/ water solution:

-the increasing of distance between needle and collector leads to the electric field decreasing, but this phenomenon cannot be compensated by voltage increasing because the modification of the needle-collector distance influences the electric field shape; needle-collector distance determines the electric field nature: a bigger value of distance has as effect a better uniformity of fibrous layers formed on collector surface;

-the feeding speed of the polymer solution is directly proportional with equipment productivity when the electrospinning process is optimum, and there are obtained fibers with no defects from the polymer solution;

-the feeding speed depends on the cross section size for the capillary, electric field intensity and polymer solution viscosity and also on the design type of the feeding device;

-the delivery speed of fibers is influenced by the electric field power and solution viscosity but also by other parameters specific to the solution, as conductivity;

-high values for capillary diameter allow high feeding speeds, in this case the processing needs an increase of applied voltage together with electric field intensity.

Conclusions

The experimental researches presented in this paper allow us to formulate the following conclusions:

-the electrospinning equipment originally designed and realized allows the obtaining of fibers at nano scale during a stable technological process;

-the computerized electrospinning equipment allows the obtaining of nanofibers from polymer solutions through systematic variation of a great number of parameters which influence the electrospinning process and the obtained fibers structure and characteristics;

-the determination of nanofibers properties requires the previous knowledge of the following polymer solution characteristics: molecular mass, the molecular mass distribution, viscosity, conductivity, electric constant, superficial tension, and density of the polymer solution;

-the computer from the command and control unit of this equipment, through its hardware and software components, controls all devices and assures the programming and the good functioning of the electrospinning process by acting upon the high-voltage power supply (applied voltage), pumping seringe (flowing speed), rotary collector engine (collector speed), and mobile nozzle engine (nozzle moving speed).

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