Control of Nanofibers Production Process Through Electrospinning

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The electrospinning technological process occurs under the influence of a plurality of factors chosen by the specialists for the evaluation of the correlation between the specific result as the effect of the process (nanofibers with special destinations) and its causes. The application of the statistic control in the electrospinning process is a premise for the production of highly uniform nanofibers with pre-established characteristics. The utilization of statistic control permits the evaluation of the state of static and dynamic stability, with significant implications in nanofibers quality. The polyetherimide-based nanofibers were obtained with modular electrospinning equipment, using as solvents dimethylacetamide, tetrahydrofuran and dimethyl sulfoxide. The values of fibers diameters were statistically processed, with the aim to improve the processing quality and to reduce the variability of technological electrospinning parameters.

Keywords: *electrospinning, nanofibers, polyetherimide, diameter, uniformity, SEM*

Electrospinning is the nanotechnology situated on top of the scientific concerns at the world level in the textile field. Given its infinite research space, the electrospinning provides the production of nanofibers utilized in a great deal of applications of interest which respond to the solution of some stringent social needs [1-5]. Electrospinning technology implies passing a polymer solution or a smelting through a nozzle (fig. 1).

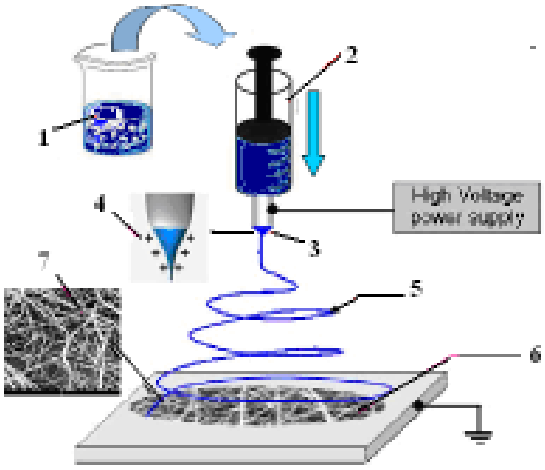

Fig. 1. Basic diagram of an electrospinning equipment: 1. polymer solution; 2. syringe with polymer solution; 3. needle; 4. Taylor cone; 5. electrospinning jet; 6. plan collector; 7. fiber mesh

The capillary's tip plays the role of electrode to which one applies a high voltage of up to 50kV. The applied voltage results in the deformation of the jet in the shape of a cone along the deposition direction. Fibers shape and dimensions depend on a various range of parameters regarding the properties of the polymer, polymer solution or electrospun smelting, environment parameters, as well as constructive and technological parameters [6, 7].

So far, many models of electrospinning equipment have been developed. They differ by: degree of automation [8-12] electrospinning process, the nature of the electrospun raw material, type of feeding, [13-16], fibrous mats type, the constructive type of the delivery mechanism [17-20], the presence or absence of needles in the composition of the delivery mechanism (with needle, [21-26], without needle, [26-28]), processing characteristics of the environment, the destination and the structure of the obtained nanofibres, [29-32].

Regarding of computerized equipment, the trend is the modularization of the electrospinning equipment, introducing new elements in the composition of different mechanisms of such equipment. There is a multitude of models proposed by the previous researches, developed and reported internationally: electrospinning classic equipment of polymer solution, multijet delivery mechanism (3jets), collecting mechanism - rotating drum, [33, 34]; Balguid [35] ensured the first view on the conception of a computerized electrospinning mechanism; Patra, [33] computerized equipment, standard atmosphere [36, 37]. Elmarco of Liberec computerized electrospinning equipment without needle, (Nanospider) – technology that produces fibrous nanostructures with diameters ranging from 200 to 500nm, on industrial scale, [38, 39]; X. Yan computerized equipment controls the flow rate of the polymeric solution, the voltage of the source [40, 41]; another study [1] constant current electrospinning equipment - proportional - integral control - derivative (PID) in which the PID parameters are set manually.

The present work proposes the realization of electrospun fibers of PEI mixed with various solvents in order to obtain nanofibers. The factors involved in this process can contribute to the realization of nanofibers whose characteristics are in agreement with the required specifications, but which, under certain limit conditions, can represent sources which generate flaws or non-conformities [42]. The values of fibers diameters have been statistically processed in order to improve the spinning process qualities and to reduce the variability of technological parameters.

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	UM	DMAcA	THF	DMSO
Molar mass	(g mol^{-1})	87.12	72.11	78.13
Density	(g/mL)	1.156	1	1.1
Viscosity	(10^{-3}Pa· s)	1.956	0.461	1.996
Boiling Point	(°C)	164	66	189
Melting Point	(°C)	-20	-108	19

Table 1
SOLVENTS USED IN PEI POLYMERIC SOLUTIONS

Polymer concentration (wt%)		Solvents	Ratio	Hansen solubility parameters				Solubility		
				δ_d	δ_p	δ_H	d			
1.	8	DMAc/THF	1:1	16.8	8.6	9.1	5.68	<	6	soluble
2.	10	DMAc/THF	1:1	16.8	8.6	9.1	5.68	<	6	soluble
3.	12	THF/DMSO	1:1	17.6	11.05	9.1	5.28	<	6	soluble
4.	12	DMAc/THF	1:1	16.8	8.6	9.1	5.68	<	6	soluble
5.	12	DMAc/THF with 1 drop DMSO	1:1	18.9	11.8	10.3	4.6	<	6	soluble
6.	12	DMAc/THF	1:1	16.8	8.6	9.1	5.68	<	6	soluble

Table 2
HANSEN PARAMETERS FOR EXPERIMENTED POLYMER SOLUTIONS

Experimental part

Materials *Polyetherimide* (abbreviated PEI and commercial name ULTEM) was used for polymer solution. It has the following characteristics, [43]: molecular weight M_w = 39000g/mol; transition temperature (Tg) of 217°C; tensile strength up to 200°C; tensile strength 105MPa; elongation 60%; compressive strength 150MPa; dielectric stiffness 27kV/mm; dielectric constant 3.15; surface resistivity higher than 13Ω; specify weight 1.27N/m^2; contraction coefficient 0.007; water absorption 0.25 - 1.25%. Polyetherimide, in various concentrations (8-12%) was mixed with a series of solvents mixtures. The solvents which we tried are Dimethylacetamide (DMAcA), Tetrahydrofuran (THF), Dimethyl sulfoxide (DMSO). Solvents characteristics are presented in table 1.

Preparation and characteristics of the blend solutions

PEI was dried for 2 h at 100°C inside a vacuum oven. In order to test the PEI solubility in mixtures of considered solvents (DMAc/THF, THF/DMSO, DMAc/THF with 1 drop DMSO), the polymer solutions were prepared by dissolving PEI in solvent mixtures under intensive stirring at elevated temperature (up to 50°C) for 24 h. Polymer solutions with different PEI concentrations (8- 12%) were obtained. The values of Hansen solubility parameters have been calculated for each solution apart. Hansen solubility parameters are presented in table 2.

From table 2 one can see that all the studied mixtures provide the PEI polymer solubilization for electrospinning.

Nanofibers electrospinning device

The equipment used in experiments is automated, with uniaxial feeding/delivery (three spinning heads), ensuring a multilayered deposition with needles and a plane collecting mechanism. The equipment has the capacity to perform the setting of the electrospinning technological parameters, being based on the idea of modularity and automated control of electrospinning process [43 - 46].

Conditions of Electrospinning

The prepared solutions have been experimented on the electrospinning system. A 2mL syringe with a 10mm diameter and an inner diameter of the needle 0.2mm 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. The distance between the capillary and the collector respectively the feeding speed were constant (D = 100mm, Q = 0.05mL/min).

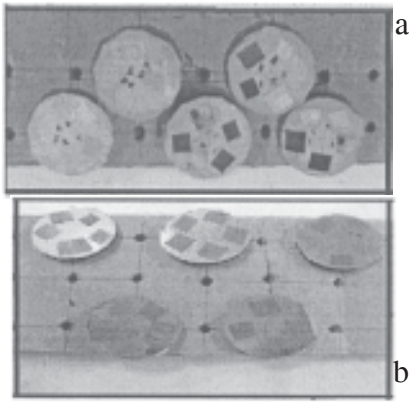

Fig. 2. Sample preparation for SEM analysis: a - before gold plating; b - gold plated fibrous deposits

Nanofibers preparation through electrospinning

The obtained polymer solutions have been processed through electrospinning on automated equipment with uniaxial feeding, single layer deposition and multijet delivery, with needles and plane collecting mechanism.

Sample preparation for Scanning Electron Microscopy (SEM).

The morphology of the electrospun nanofibers was inspected with a Scanning Electron Microscope FEICO (Model Phenom G2). The properties of nanofibers membrane as fiber diameter were determined by using Nis-Elements and Lucia software. In order to take up better the images at the scanning electron microscope such that to highlight in details the surfaces of the analyzed samples, we proceeded to gold plating of the fibrous surfaces (fig. 2a) using the Tesla SCD equipment presented in figure 2b.

Results and discussions

Parameters of computerized electrospinning system are presented in table 3.

The capacity of electrospinning equipment to maintain in time the values of its technological parameters both in terms of adjustment (position with respect to the center of the technologically accepted variation interval), as well as in terms of precision (position with respect to the limits of the interval) reflects its performances, [47, 48]. What concerns the electrospinning equipment or installations, there are still a series of uncertainties with respect to [49-59]:

a. adjustment stability and precision of technological parameters during the process development;

Polymer concentration (wt%)		Solvents	Ratio	Parameters of electrospinng					
				Distance (mm)	Voltage (kV)	Temp. (^{0}C)	Humidity (%)	Average diameter d (nm)	C_V (%)
P1.	8	DMAc/THF	1:1	100	20	25	35	142.45	24.95
P2.	10	DMAc/THF	1:1	100	22	25	32	167.48	23.31
P3.	10	THF/DMSO	1:1	100	20	20	35	195.69	29.59
P4.	12	DMAc/THF	1:1	100	22	24	35	373.22	27.32
P5.	12	DMAc/THF with 1 drop DMSO	1:1	100	25	25	39	182.67	20.64
P6.	12	DMAc/THF	1:1	100	25	24	32	487.16	29.15

Table 3
ELECTROSPINNING PARAMETERS AND THE VALUES OF ELECTROSPUN FIBERS DIAMETERS

b. the manner in which disturbances generating flaws and/or non-conformities appear in the realized nanofibers;

c. possibility to generate successive nanofibers samples with known characteristics; ruling out these uncertainties can be offered by the statistical control of the process.

The technological parameter control implies various stages which include the initial adjustment control (at the beginning of the electrospinning process) of the electrospinning equipment (static stability) and the control of dynamic stability degree of their values (during equipment operation) respectively, [53-59]. A process is considered statically stable if the values of its parameters are statistically distributed according to a known distribution law (usually, a normal distribution). Similarly, a process is considered dynamically stable if the statistic distribution preserves its initial shape and position all along the process. The application of the statistic control implies running through the following stages:

- selection of value characteristics by whose means the process capability will be assessed;
- verification of electrospinning process with the view to remove the causes for the appearance of possible disturbances of the process characteristics;
- statistic analysis, consisting in: carry out large volume sampling, checking up the general statistic hypotheses, assess the statistic parameters which reveal the adjustment and its precision, evaluation of knitting process capability and determination of the control (for statistic parameters of adjustment and adjustment precision) and safety (monitoring) intervals;
- the control in itself consists in: determinations (in time) of the adopted technological parameters and configuration of the final decision that can be stated in different ways, depending on the obtained results: continue/stop the process/possibility to apply some coercive forces to remediate the situation.

Running through the previous stages implied:

- choose the nanofibers diameter as control parameter;
- previously check up the values of constructive and technological parameters considered as initial through the established experimental plan.

The preliminary statistic analysis consisted in carrying out by 100 determinations of fiber diameters for each sample P1- P6. In order to verify the general hypotheses, the following tests were applied: iteration tests (to assess the random character of the sampling data); Grubbs test (to check up and remove the abnormal values); χ^2 test (to assess the concordance between the normal theoretical distribution and the studied sampling distribution).

The estimation of the statistic parameters of adjustment and precision by means of average (x) and dispersion (s^2) implied the utilization of a statistic program, on whose basis the average diameter values of the considered samples, the standard deviation and the variation coefficient have resulted.

Figura 3 presents the fibrous deposits obtained from PEI polymer solution and mixtures of solvents, samples P1-P6.

Figure 3a presents the images of the fibrous deposits obtained from polyetherimide polymer solution and mixtures of solvents presented in table 3, where P1…..P6 are the samples from 1 to 6. For all the realized samples we have obtained continuously delivered dry fibers with fiber diameters comparable depending on the adopted technological parameters and also on the variation of polymeric solution concentration.

The increase of polymeric solution concentration resulted in an increase of fiber diameters. In the fibrous deposits obtained from PEI 12% DMAc/THF1:1, 12% polymer solution, P4, the appearance of beaded structural defects was recorded. Most probably, their appearance was due a high instability of polymeric solution produced by a high evaporation rate and a large applied voltage.

Table 3 presents the values of the mean diameter d(nm) calculated with the relation:

$$d_{med} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad (1)$$

where n represents the number of determinations, and x_i = the values of fibers diameter.

The value of the variation coefficient C_v% was calculated with the relation:

$$Cv = \frac{\sigma}{d_{med}} \cdot 100 \quad (\%) \qquad (2)$$

where σ represents the mean square deviation.

From the comparison of the coefficient of variation of the nanofibers diameter values, one can appreciate that, for the technological values P1, P2, P5 one obtains smaller C_v values of the fibers diameter, which means that for these polymer solutions, under the specified experimental conditions, the variability of the analyzed characteristic is smaller and the technological process is more stable.

The distribution histograms of the frequencies of the fibers diameters values are plotted in figure 3b. The analysis of the frequency histograms from figure 3b shows that:

-for the samples P4 the frequency histograms present left asymmetry;

-sample P6 shows a quite good symmetry, but a large dispersion of the fiber diameters values;

-samples P1, P2 present histograms with high frequencies values in the central zone of the diameters values; these can be approximated by Gauss- Laplace curves;

-in the case of sample P2, the frequency polygon presents a single maximum in the central zone; it can be

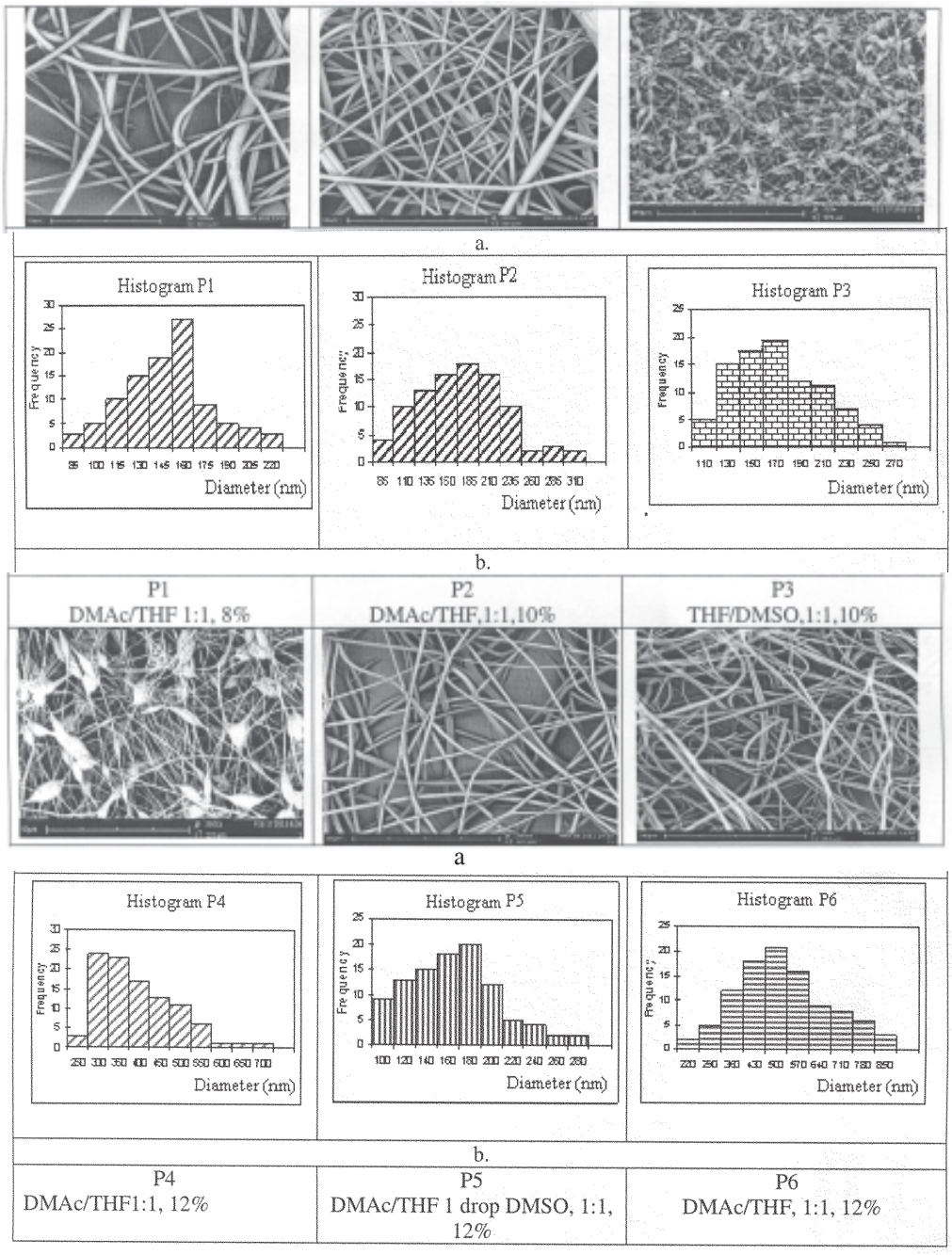

Fig. 3. The fibrous deposits obtained from PEI polymer solution and mixtures of solvents, samples P1-P6: a. SEM images of nanofibers (x500); b. the distribution histograms of the frequencies of the fibers diameters values

approximated with the normal distribution, but the variation coefficient has a bigger value.

Grubbs' Text detects the outliers from normal distributions. Each sample was tested with Kolmogorov-Smirnov test for normality with significance level (α) equal with 0.05.

The extreme values (maximum value x_{max}, minimum value x_{min}) found in the experimental data sets for samples P1- P6 were tested with Grubbs' Test. A significance level as 0.05 was adopted. The procedure is the following:

-write the two hypothesis:

Ho: x_{max} / x_{min} is not outlier in the data set;

H_1: x_{max} / x_{min} is an outlier in the data set;

-write the computed sample mean and standard deviation for each data set,

-compute the specific statistical value for Grubbs' Test (g_c):

$$g_c = \frac{x\,max - \bar{x}}{s} \text{ or } g_c = \frac{\bar{x} - x\,min}{s} \qquad (3), (4)$$

where:

$\bar{x}$ and s mean the sample arithmetical mean and standard deviation.

The values g_c are compared with the given value $g_{100;\,0.05}$ = 3.207. If the computed value g_c is less than the given value $g_{100;\,0.05}$ the extreme value may remain in the data set (this means that the hypothesis Ho is accepted with a probability of 1-α = 0.95).

Conclusions

The statistic control is an important step in improving the quality of the process of nanofibers generation, in finding some constructive and functional developments of the equipment, in order to reduce the variability of the technological parameters, with implications on the characteristics of electrospun fibers.

The results of this study have showed with a probability p = 0.95% that the sampling distributions for the samples P1, P3 have a random character, which implies in their case the existence of a well - conducted technological processes. The other technological variants present large dispersions of the fiber diameter values and frequency histogram asymmetries, aspects which reflect the existence of process disturbances.

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