Electrospinning of Polyetherimide (PEI) Solution

Effect of nozzle sizes on the diameter of the fiber

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The transversal dimension of electrospun fibers depends on a multitude of technological, constructive and environment factors and not finally, on the characteristics of polymeric solution. This study has examined the effect of the nozzle sizes on the diameter of the fibers of 12% polyetherimide (PEI) solution using as solvent dimethyl acetamide /tetrahydrofuran (DMAC/THF), 1:1 ratio. The polymer solution was processed at two values of nozzle size, and the voltage, feed rate and spinning distance were also varied. Processing with different parameters resulted in the production of fibers with diameters varying between 208 and 738nm. When the diameter of the nozzle size of the needle decreases, the surface tension of the drop increases and diminishes the resulted fibers diameter.

Keywords: electrospinning, nanofibers, PEI, nozzle size, *fiber diameter*

By electrospinning, one obtains fibers of nanometer size used to manufacture innovative materials with various applications: drugs delivery, tissue scaffolds, wound dressing [1,2], tissue engineering, filtration, semiconductor nanowire synthesis, sensors, bioseparation applications [1-5], protective clothing, reinforcement in composite materials etc. The electrospinning process is complex due to the multitude of factors that interfere in the process [6-9], which determines peculiar behavior of each polymeric solution apart [10-14]. Getting dry fibers free of bead in a stable continuous process is the result of preliminary investigations meant to find adequate intervals for the values of each technological, constructive and environment parameter [15-17].

In absence of disturbances determined by the high values of the formed electric field, the jet is positioned vertically on the collecting surface (axially-symmetric jet). Near the collecting zone, this axially symmetric delivered jet deviates from its axis, thus defining a so-called bending instability. Even in the condition of electrospinning processing of the same polymeric solution, with the same technological, constructive and environmental parameters, the shape of the delivered jet is not identical. The random appearance of these process disturbances makes difficult mathematical modeling of jet shape [18-21]. While the probability of jet disturbance appearance is the same all along its way between the needle and the collector, the electrohydrodynamic instability phenomenon only appears at a certain distance from syringe top, after a linear travel. The factor with major influence which results in the appearance of the so-called "critical point" from which the instability phenomenon appears is given by the decrease of the bending stiffness of the polymeric jet [22-26]. This diminution of bending stiffness is determined by the decrease of polymeric jet diameter occurred with the jet moving away from the needle and getting closer to the collector. Bending stiffness is given by the relation:

$$R_i = E \cdot I,$$

where

$$I = \frac{\pi}{64} d^4 = \frac{\pi}{4} R^4$$

R is the radius of delivered jet, mm;

E - Young modulus.

The surface tension of the polymeric liquid opposes to the forces which determine the bending instability phenomenon, because jet bending in itself always result in an increase of jet surface. Therefore the instability phenomenon starts when the force which determines this phenomenon is bigger than surface tension of polymeric liquid [27-30]. The researches undertaken on the instability phenomenon manifested during jet electrostatic formation have identified three different types of instabilities [31]: axially-symmetric instability whose value dominates the Rayleigh instability, expansion instability, both being due to electric charges; non-axially symmetric bending instability. The disturbances appeared in jet shape and in its spraying way influence the characteristics of the delivered jet, namely: its radius, jet displacement speed, electric field value, density of surface charge [32-33]. Bending instability occurs when the polymer jets become thin enough and the nanofibers quickly twirl. The large length of the resulted polymeric contour determines a bigger stressing rate and a nanometric diameter [34-36]. In this case, an increase of the applied voltage results in the increase of the length of linear axial zone and therefore the angle of the spiral formed by the bending instability phenomenon. The formation of some spiral surfaces from the polymeric jet determines the appearance of instabilities in the point characterized by the biggest curvature of jet surface, the point where the wave length is maximal. Therefore this instability leads to a loosening (side branching of the initial jet). The non-axially symmetric instability (asymmetrical) is responsible for the subsequent appearance of those successive bendings, (whipping instability) which determines a successive modification of the jet form and has two stages [37-40]:

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- phase I, the onset, when small fluctuations appear laterally from the initial jet axis, fluctuations which induce in the jet a distribution of bipolar charge that interacts with electric field which results in its tilting;

- phase II, which appears as a mutual rejection of the charged surface carried by the jet, which results in effective jet bending.

The bending instabilities of the charged jet are far from being controllable or reproducible. Twirling motion of the jet changes its amplitude and it is randomly projected. This behavior is different, being defined as whipping instability, typical for viscous jets gathered on the plane collector. That is why the structure of a collected nanostructure is usually very irregular, and special focusing techniques are necessary to obtain ordered fibrous network.

In order to reveal the main factors acting on the electrospinning in general and on the way the jet is initiated especially, it is important to evaluate two global characteristics, namely:

-the length of straight jet trajectory prior to the appearance of hydrodynamic instability;

-initial angle of loops envelope.

Appearance of electrospinning processing instabilities is highly conditioned by the value and uniformity of the applied electric field, local temperature fluctuations at the liquid surface, collector constructive type, applied electrostatic potential, characteristics of polymeric solution (viscosity, solvent evaporation rate etc.).

For each polymeric solution and each set of electrospinning parameters there is a *limit value 1* for the generation of bending instability at a certain value of the applied electric voltage. The subsequent increase of the applied electric potential lengthens the straight line trajectory of the jet and results in the formation of large, relatively stable loops. The initial bending is almost perpendicular to jet direction. When going beyond another *limited value 2* of the applied electric field, the angle of the spiral envelope decreases, while the length of the straight segment of fiber keeps increasing. A slight diminution of polymer solution concentration can determine large amplitude of oscillation of the length of the straight segment. Subsequent investigations are necessary to elucidate the nature of these unstable interactions appeared in the onset phase of electrospun polymer jet.

The present work analyses the influence of the nozzle size on the diameters of nanofibers from solutions of 12% polyetherimide (PEI) using as solvents dimethyl acetamide/tetrahydrofuran (DMAC/THF), 1:1 ratio. The shape of the initial jet and the way of Taylor cone generation depend on the nozzle size [41-43]. Researches undertaken on polymer solutions show a direct proportionality between nozzle size and nanofiber diameter [44-45].

We consider that, among the factors, which influence the electrospinning process, the electric field strength, E, kV/cm is a complex parameter, as it represents the ratio between a technological parameter - applied voltage, U, kV and a constructive parameter, spinning distance, D, cm. The increase of the applied voltage modifies the drop shape [45-47] and, depending on the polymer type and the selected values of spinning distance, the transversal and longitudinal dimensions of the fibers can decrease [48] or increase [3, 17-19, 48-57].

The study carried out in this work concerned the variation of voltage, needle-collector distance, feed rate and nozzle size, in order to study the considered influence in the case of processing a polymeric solution of polyether amide (PEI) in concentration of 12%, using as solvent dimethyl acetamide/tetrahydrofuran (DMAC/THF), 1:1 ratio.

Experimental part

Materials

Spinning solutions of PEI were prepared by dissolving the polymer polyetherimide with molecular weight M_w = 39000g/mol, (12%) in solvent mix (DMAC/THF), 1:1 ratio. The polymer was dried at 100°C for 2h, and then solved at 50°C for 24h in solvents mix [17, 18, 51].

Electrospinning experiments

Nanofibers electrospinning was carried out with an equipment providing a continuous process, which realizes the electrospinning from solution with needle, delivery mechanism with nozzle and a collecting mechanism of rotating cylinder type connected to ground, where the speed v= 1000rpm [17, 18, 58 - 61]. The fibers obtained by electrospinning the polymeric solution of PEI were collected on dark paper on which the electrospun web was obtained. We have used syringe with a volume of 3mL, with inner needle diameter Ph_i = 0.2mm and 0.3mm, number of syringes = 3, inter-nozzle distance 2.5mm, interval of displacement along Ox axis, x = 100mm; interval of displacement along Oz axis, z = 80mm [3, 17, 18]. Processing environmental conditions were 20°C, U = 40% under normal atmospheric pressure. The values of the studied spinning distance D were D = 70mm, D = 100mm and D = 120mm. Determinations were performed at four consecutive values of the flow rate Q, mL/min, namely 0.05mL/min, 0.075mL/min, 0.1mL/min and 0.15mL/min. The voltage was varied within the interval 15÷35kV, namely U = 15kV, U = 20kV; U = 25kV, U = 30kV, U = 35kV, such that the resulted electric field strength ranged between 1.25÷7.78kV/cm. In the following, only four values of the electric field strength have been considered, namely 2.92kV/cm, 3.50kV/cm, 5.00kV/cm and 7.78kV/cm.

Characterization of the mix solution

The surface tension of the PEI/DMA/THF polymer solution was measured with Krüss K9 equipment. The polymer solutions conductivity was determined with the Eurotech Chromoservis 510 conductometer. The viscosity of the polymeric solution was measured by using the Gemnini Rotational 2 Rheometer with two functions of this equipment: viscometry and oscillation.

Scanning Electron Microscopy (SEM) analysis FEICO was used to view the fibers. In order to determine the fibers diameters from working variants of SEM images, Nis-Elements and Lucia software were used. In order to estimate the effect of nozzle size on the fibers diameter, it was necessary to determine the fiber diameter for each set of values of the considered technological and constructive parameters. 100 measurements of fiber diameter were performed for each working variants, necessary for the calculation of the mean values of fiber diameter and the standard deviation, nm.

Results and discussions

The determined mean value of the surface tension of 12% polyetherimide solution in solvents mix (DMAC/THF), 1:1 ratio was 30.3mN/m. The surface tension value is determined by the solvent type and the concentration of polymeric solution; its value determines the electrospinning upper and lower limits under the condition that all the other process variables are constant [51]. It has been experimentally noticed that a smaller value of the surface tension leads to the formation of fibers without beads [17, 18]. The determined mean conductivity of the polymeric solution was around 1.18mS/cm. The mean viscosity of polymeric solution was around 0.191Pas. The polymeric

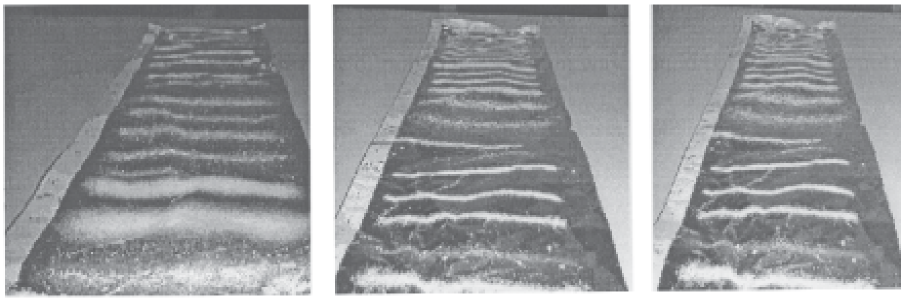

Fig.1. Appearance of PEI nanofibers on dark fibers at difference values of electric field strengths

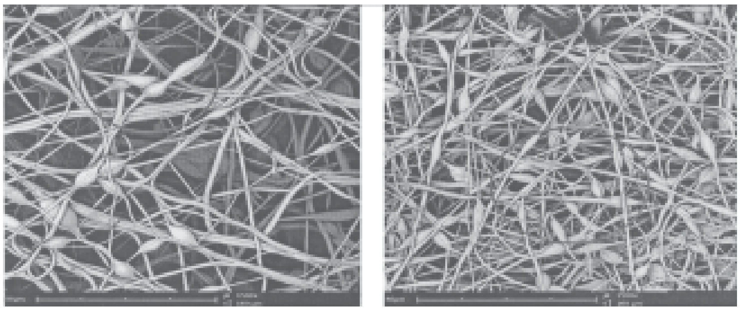

Fig. 2. SEM images of fibers of 12%PEI, with (DMAC/ THF), 1:1 ratio, processed on electrospinning equipment with Q = 0.15mL/min:
a. D = 100mm and U = 15kV; b. fibers stuck and with drops, D = 120mm and U = 35kV

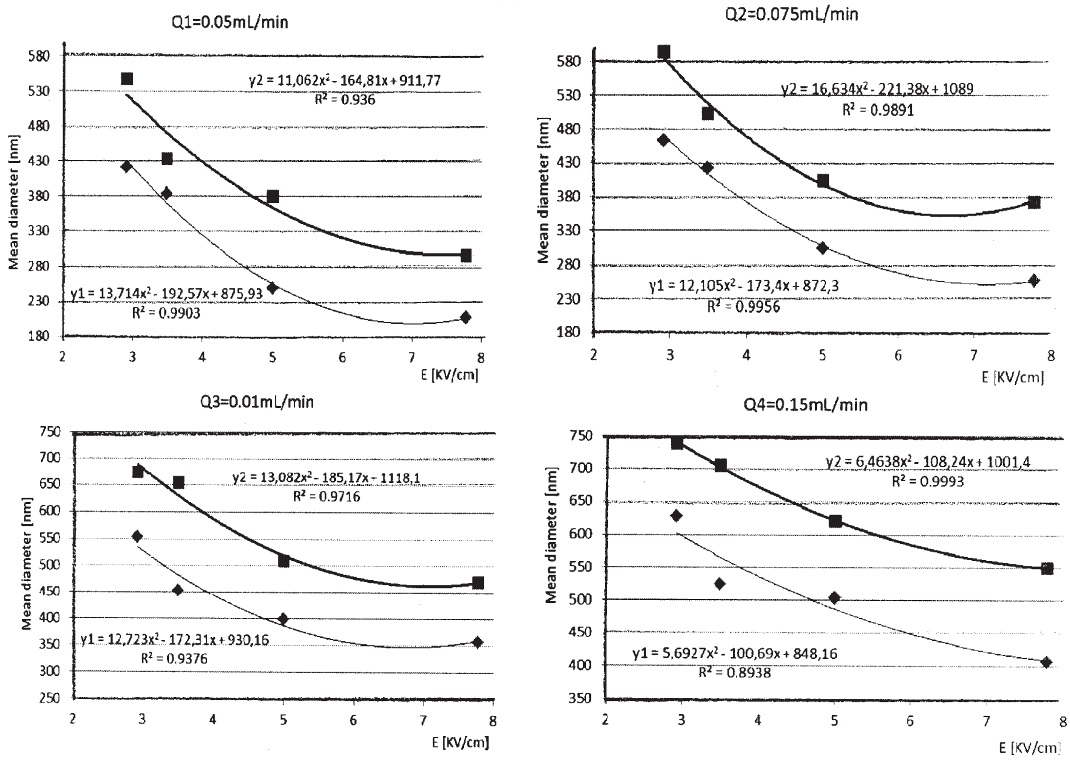

Fig. 3. Fiber diameters of PEI 12wt%/DMAC/THF, 1:1 ratio solution electrospun using different nozzle sizes (♦ Phi = 0.2mm, trendline y_1; ■ Phi = 0.3mm, trendline y_2):
a. Q1 = 0.05mL/min,
b. Q2 = 0.075mL/min,
c. Q3 = 0.1mL/min,
d. Q4 = 0.15mL/min)

solution viscosity has a major influence on the fiber diameters, a bigger viscosity resulting in the generation of fibers with larger diameters [1, 17, 18].

Formation and deposition of electrospun web was performed on dark paper, each sample being numbered according to the working variants. Figure 1 presents the appearance of PEI nanofibers on dark paper at different values of electric field strengths.

Fibers diameter and morphology are influenced by the processing technological conditions. Processing the polymeric solutions of polyetherimide in concentration of 12% / (DMAC/THF), 1:1 resulted in the production of fibers with diameters ranging between 208nm and 738nm. Figure 2 presents the SEM images of fibers corresponding to two technological variants.

What concerns the electrospinning processing of PEI polymer, from the experiments carried out with needles with inner diameters of 0.2mm and 0.3mm respectively, it resulted that a smaller needle inner diameter reduces the clogging of capillary tip, thus diminishing the amount of drops distributed on electrospun fibers deposited on collector. In the case of electrospinning processing with needles with inner diameter of 0.2mm, at the same value of the applied voltage, a much higher Coulombian force is necessary in order to form a polymeric solution jet; the size of the drop from the needle point orifice decreases, and the surface tension of the drop increases accordingly.

At the same flow rate value, with the modification of nozzle size 0.2mm to 0.3mm, bigger fiber diameters were obtained (fig. 3). This figure illustrates the effect of nozzle size on electric field strength and fiber diameter respectively, at constant flow rate values. At the same flow rate value, the smaller is the needle inner diameter, the higher is the surface tension of the drop and the smaller is the fiber diameter.

Figure 3 gives also the regression equations and correlation coefficients corresponding to the dependence between electric field strengths and electrospun fiber diameters.

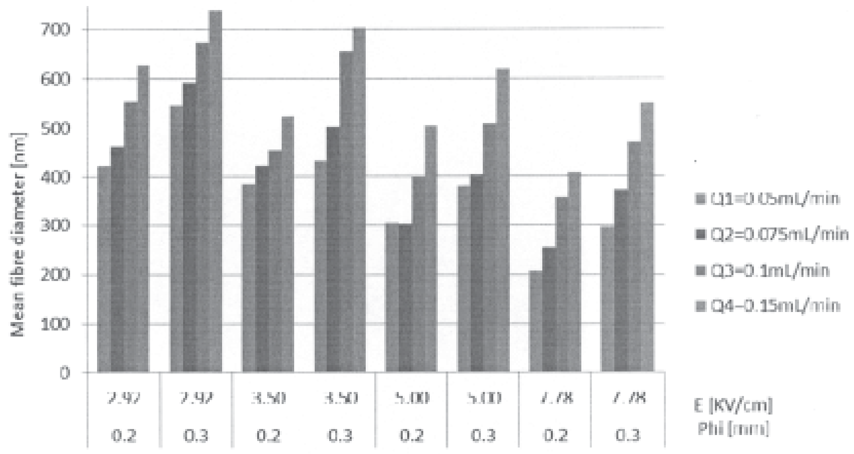

Fig. 4. Effect of nozzle size on the diameter of the fiber

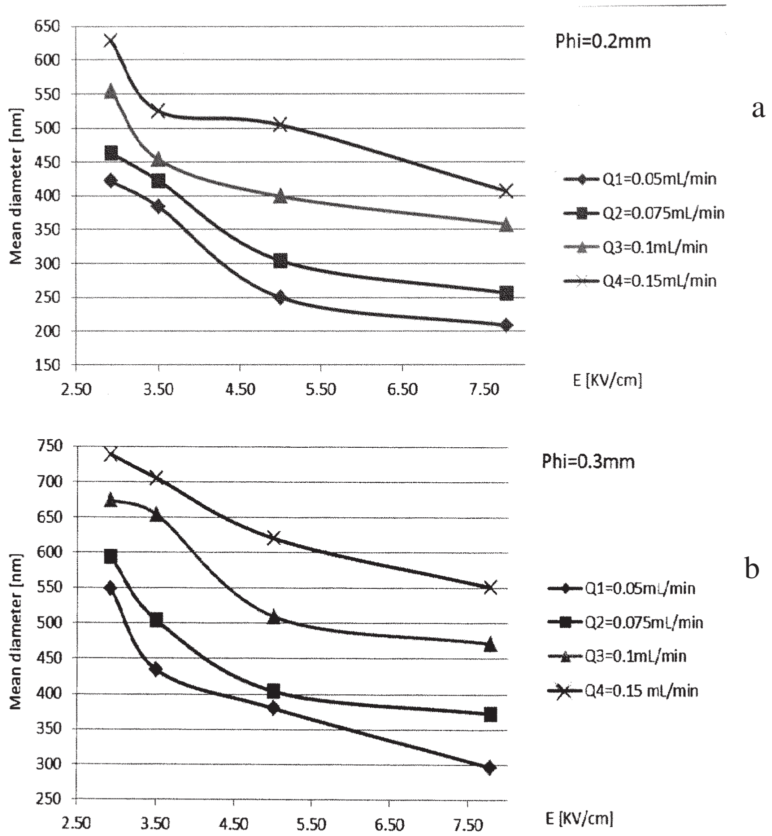

Fig. 5. Effect of the electric field strengths on the diameter of the fiber: a. Phi = 0.2 mm; b. Phi = 0.3 mm

At the same flow rate value, the fiber diameter values decreases with the increase of the electric field strengths, regardless the size of nozzle inner diameter (fig.4).

Figure 5 presents the influence of the electric field strengths on fiber diameter at the same flow rate values in the cases of nozzle sizes Phi = 0.2mm (fg. 5a) and Phi = 0.3mm respectively (fig. 5b). The data points are connected with smooth lines (Spline functions) that best fit through all of them. It appears that, for the same value of the electric field strength, the increase of the flow rate value determines the generation of fibers with smaller diameters.

At the same electric field streangths value, increasing the flow rate leads to fibers with smaller diameters.

Conclusions

This study has investigated the electrospinning of polyetherimide solution and the effect of nozzle size on the fiber diameter. The technological (applied voltage, supply rate) and constructive (spinning distance, nozzle size) parameters have been varied. Fibers were produced through electrospinning at consecutive values of electric field strength, E, kV/cm and different values of nozzle size. The SEM images and fiber diameter values have been studied.

At the same value of the flow rate, with the modification of nozzle size from 0.2mm to 0.3mm, bigger fiber diameters were obtained. When the diameter of the nozzle orifice of the needle decreases, the surface tension of the drop increases and diminishes the resulted fibers diameter.

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