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Influence of the Shape of the Bottom Rotating Electrode on the Structure of Electrospun Mats

Abstract
In this study nanofibres from poly(vinyl alcohol) (PVA) and thermoplastic polyurethane (TPU) polymers solutions were manufactured using the electrospinning method (Nanospider^{TM}). During the electrospinning process, three different bottom rotating electrodes were used (spinning head):a plain cylindrical electrode and two different electrodes with tines. During the experiments, mats were manufactured from PVA nanofibres using all three types of electrodes. The structure of the electrospun PVA mats varied with a change of spin electrode. During the experiments, porous mats from TPU nanofibres were formed only using electrodes with tines (it was not possible to form TPU nanofibres using a plain cylindrical electrode). The shape of the bottom rotating electrodes does not have an influence on the diameter of electrospun PVA or TPU nanofibres.

Key words: *electrospinning, nanofibre, PVA, TPU.*

Introduction

The past decades have witnessed tremendous progress in the development of the electrospinning technique due to the wide applications areas of the products obtained. Electrospinning is a simple and versatile method of generating ultrathin fibers from a rich variety of polymers. Electrospun polymer fibers span more than four orders of diameter magnitude, with nanofibres having cross-sections containing fewer that 10 elongated polymer molecules at one end of the range and conventional textile fibers at the other [1-3].

Electrospinning is easily realised by applying a high voltage to a capillary filled with the polymer solution to be spun with the help of an electrode. Fibres formed are collected on a grounded plate, which can be covered, for example, with some fabric. Research groups working on nanofibres use different types of electrospinning apparatus. The apparatus usually has a capillary with the polymer solution perpendicular to the grounded plate. Sometimes the capillarity can be pointed at a certain angle to the grounded plate. The collector is usually a plain metal sheet, but it can be a rotating cylinder, disc collector, parallel electrodes, or grounded rings [4-11].

The following parameters and processing variables affect the electrospinning process: (i) the type of polymer, and polymer solution parameters, such as the molecular weight of the polymer, viscosity, conductivity, and surface tension of the polymer solution, (ii) process parameters – flow rate of the polymer solution, applied voltage, and the distance between electrodes, (iii) ambient parameters – temperature, humidity and air velocity in the electrospinning chamber [1, 7, 12]. There are a lot of references concerning the influence of polymer solution properties and electrospinning process parameters on the structure of the electrospun mat formed, but there is a lack of information about the influence of the type of electrospinning apparatus on the structure of electrospun mats. W. Tomaszewski and coauthors performed tests on three types of electrospinning heads: series, elliptic and concentric. Results showed that the latter two allowed the process to proceed on the basis of compact multijet systems using 10 or more spinning pipes. The efficiency and quality of the process were the best using a concentric electrospinning head [8]. F. Cengiz and coauthors electrospun polyacrylonitrile (PAN) nanofibres using three different electrospining apparatuses by conventional methods – Jirsak's method, and Yarin and Zussman's method [13]. Analysing the results presented, it is possible to notice that the diameter of electrospun PAN nanofibres is different for every electrospinning setup.

Poly(vinyl alcohol) (PVA) is a hydrophilic polymer of excellent chemical and thermal stability, and it is a biocompatible and non toxic synthetic material that is easily manufactured by the electrospinning process [14-17]. Polyurethane (PU) nanofibres may be used in a wide variety of applications such as filters, protective textiles, wound dressing materials, and scaffolds [18-21]. Analysing literature data concerning PU nanofibres, it was noticed that it is quite difficult to form uniform nonwoven material from polyurethane nanofibres by the electrospinning process.

The aim of this study was to study the influence of the shape of the bottom rotating electrode (spinning head) on the structure of electrospun mats from PVA (easily spun polymer) and TPU (less easily spun polymer) fibers.

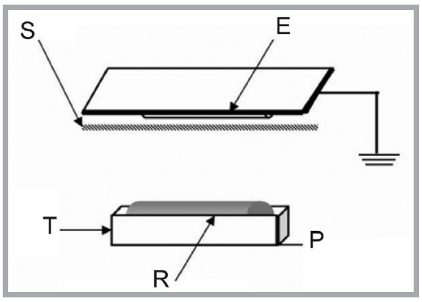

Figure 1. *Principal scheme of electrospinning equipment used – Nanospider ™ (Elmarco): E – grounded electrode (fixed), S – support material (spunbond from PP filaments), T – tray with polymer solution, P – power supply with a positive polarity of 0-75 kV, R – bottom rotating electrode (plain cylinder or electrode with tines).*

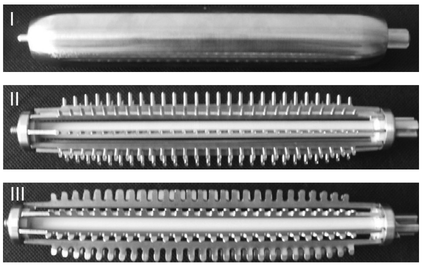

Figure 2. *Photos of bottom rotating electrodes; I – plain cylindrical electrode, II – electrode with tines (side view of tine), III – electrode with tines (side view of tine).*

Materials

Powder of poly(vinyl alcohol) (PVA) (ROTH, Germany) *M* = 72000 g/mol, granules of thermoplastic polyurethane (TPU) (Laripur, Coim Group, Italy).

Methods

Preparation of polymer solutions

PVA solution of 7% concentration was prepared by dissolving PVA powder in 70°C distilled water by magnetic stirring for 2 hours. Thermoplastic polyurethane (TPU) (Laripur) solution of 3% concentration was prepared by dissolving TPU granules in dimethylformamide and tetrahydrofuran (1:1, w/w) mixed solvent. The TPU solution was mixed for 48 hours by magnetic stirring without heating.

Table 1. *Parameters of the electrospinning process using different types of bottom rotating electrodes.*

Polymer solution	Distance between electrodes (*L*), cm	Applied voltage (*U*), kV	Current (*I*), mA		
			bottom rotating electrode I	bottom rotating electrode II	bottom rotating electrode III
PVA	12	40	0.060-0.090	0.070-0.080	0.060-0.080
		45	0.110-0.140	0.100-0.130	0.120-0.150
		50	0.210-0.230	0.180-0.210	0.180-0.220
		55	–	0.240-0.280	–
	15	45	0.004-0.035	0.016-0.060	0.030-0.068
		50	0.050-0.100	0.070-0.095	0.065-0.095
		55	0.110-0.140	0.090-0.130	0.100-0.140
		60	0.170-0.195	0.120-0.160	0.150-0.180
		65	0.240-0.260	0.180-0.210	0.180-0.230
		70	–	0.210-0.250	–
TPU	15	45	–	0.005-0.008	0.001-0.003
		50	–	0.020-0.025	0.002-0.003
		55	–	0.034-0.041	0.003-0.017
		60	–	0.050-0.054	0.016-0.038
		65	0.003-0.016	0.068-0.073	0.040-0.055
		70	0.008-0.020	0.085-0.092	0.076-0.083
	17	45	–	–	–
		50	–	–	–
		55	–	0.018-0.022	0.011-0.014
		60	–	0.040-0.045	0.015-0.023
		65	0.004-0.018	0.045-0.055	0.031-0.045
		70	0.020-0.030	0.060-0.070	0.055-0.060

Electrospinning equipment

The substratum material (spunbond from PP filaments) was covered by a layer of PVA and TPU nanofibres using a "Nanospider™" (Elmarco, Czech Republic). While rotating, the cylindrical electrode or the electrode with tines (spinning head) is covered by a film of polymer solution. By increasing the applied voltage, Taylor cones are formed. Only when an electrostatic force overcomes the surface tension of the polymer is a jet of polymer solution ejected from the Taylor cone. The jet moves toward the upper electrode and sets down on the substratum material (nonwoven spunbond from PP filaments). Meanwhile the nanofibre becomes thinner, the solvent evaporates and later solidifies (***Figure 1***) [14, 22].

In this study three types of bottom rotating electrodes were used: I – a plain cylindrical electrode, II – an electrode with tines of width (*a*) 2 mm, III – an electrode with tines of width 3 mm. Electrodes II and III are different in the shape and width of their tines (***Figure 2***).

During the experiments with PVA polymer solution, the distance (*d*) between electrodes was 12 cm and 15 cm; the applied voltage (*U*) varyied between 40 kV and 75 kV; the temperature of the electrospinning environment was t = 18±2°C, and the air humidity γ = 50±2%. During the experiments with TPU solution, the distance (*d*) between electrodes was 15 cm and 17 cm; the applied voltage (*U*) varied between 40 kV and 75 kV; the temperature of the electrospinning environment was t = 20±2°C, and the air humidity γ = 40±2%.

Characterisation techniques

The structure of the PVA and TPU nanofibres mats was determined using a scanning electron microscope (SEM) – Quanta -2000 (FEI). The diameter of PVA and TPU nanofibres was measured using the image analysis system LUCIA 5.0. All derivatives of nanofibres (single, stick) from every SEM image were measured because the structure of the mat analysed in this study was composed of nanofibres.

Results and discussion

During our previous study [22], it was noticed that when working with hard spun polymerssolutions (PVA with catonic starch), only the edges of the substratum material were covered by a layer of mat from nanofibres. Taylor cones (initiators of nanofibres) were not formed throughout the whole length of the cylindrical electrode, but only on the edges of it i.e Taylor cones first appear where there is the highest electric field – on the tip of the cylinder. In this study, three types of electrodes were used (***Figure 2***) and two types of polymer solutions chosen: (i) – easily electrospun PVA, (ii) – less easily electrospun TPU.

Table 1 presents the parameters of the electrospinning process using different shapes of the rotating electrodes, from which PVA and TPU solutions were electrospun. From the data presented, we can see that with an increase in the applied voltage (the distance between electrodes is constant), the current is increased in all cases. At distances of 12 cm and 15 cm between electrodes, using PVA solution, consequently the highest applied voltage was 55 kV and 70 kV; only then was the electrode with the smallest surface area used (II type). Using PVA polymer solution and electrodes types I or III, the equipment automatically discharged at U = 55 kV, L = 12 cm and at U = 70 kV, L = 15 cm. Hence we can conclude that the type of bottom rotating electrode has an influence on the electrospinning process in the case of easily spun polymer solution. During the test with PVA solution, no significant difference was noticed between the current values using various types of electrodes (***Table 1***).

It was not possible to form a mat from TPU solution using a plain cylindrical electrode (I), even at an applied voltage of 70 kV – the current is very small and only a few single nanofibres were possible to create. Using electrodes with tines (II and III), mats were electrospun from TPU solution. We can make the assumption that when we use electrodes with tines (II or III), higher electrostatic forces are created (due to the narrow tines), which can overcome the surface tension of TPU solution; therefore it is possible to form TPU fibres.

From the SEM images presented in ***Figure 3***, it is possible to notice that by changing the type of bottom rotating electrode, the structure of the electrospun PVA mat is altered. Denser mats are formed using a cylindrical electrode (I type) at an applied voltage of 50 kV. With an increase in the surface area of the electrode, more Taylor cones are formed and denser mats from PVA nanofibres cover the support mate-

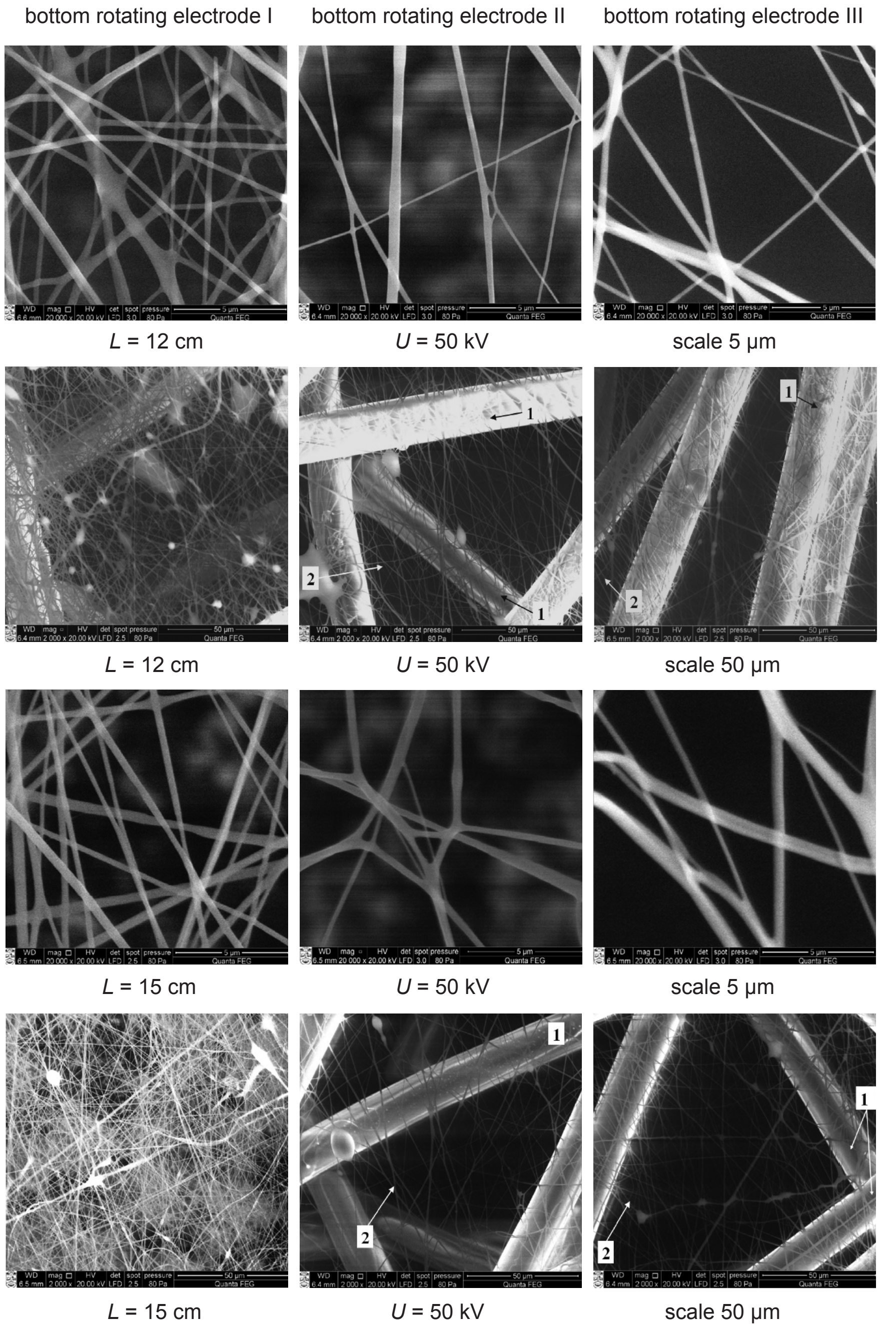

Figure 3. *SEM images of electrospun PVA mats using different type of rotating electrode, the distance between electrodes (L) 12 cm and 15 cm, applied voltage (U) 50 kV: I cylindrical electrode, II, III electrodes with tines (number 1 indicate filaments of support material – spunbond from PP filaments, number 2-electrospun mats from PVA nanofibres).*

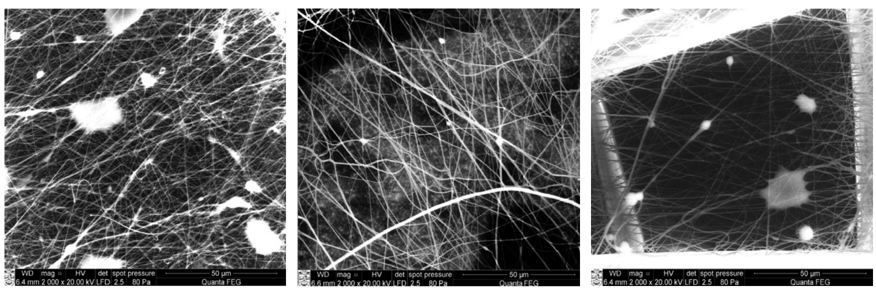

Figure 4. *SEM images of PVA mats electrospun at an applied voltage (U) of 65 kV, distance between electrodes (L) – 15 cm; from left to right: I – plain cylindrical electrode, II, III – electrodes with tines.*

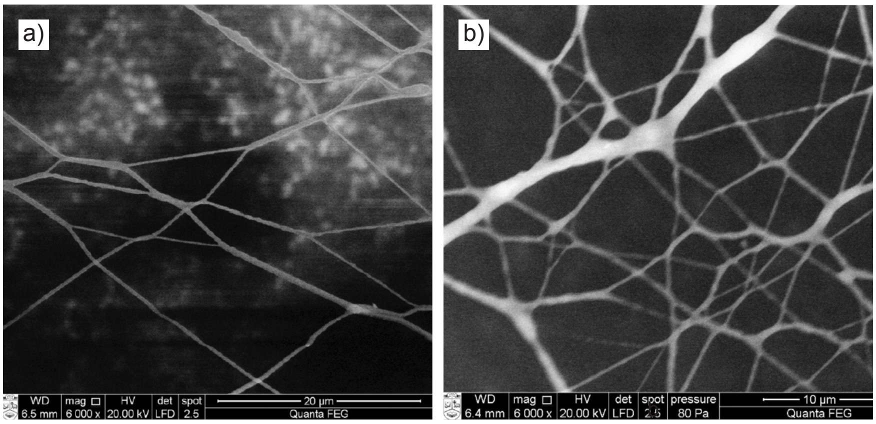

Figure 5. *SEM images of TPU mats electrospun at a distance between electrodes (L) of 17 cm and applied of voltage (U) 65 kV: a – electrode II, b – electrode III.*

Table 2. *Average nanofibre diameter using different types of bottom rotating electrodes.*

Polymer solution	Distance between electrodes (*L*), cm Applied voltage (*U*), kV	Method of calculating average nanofibre diameter	Average diameter of PVA nanofibres, nm		
			bottom rotating electrode I	bottom rotating electrode II	bottom rotating electrode III
PVA	12 cm, 50 kV	A*	300±25	310±40	300±45
		B*	270±18	280±30	220±30
PVA	15 cm, 50 kV	A*	290±25	300±40	330±45
		B*	270±20	260±30	270±30
PVA	15 cm, 65 kV	A*	300±25	380±70	320±40
		B*	260±18	290±40	250±20
TPU	17 cm, 65 kV	A*	–	470±40	550±70
		B*	–	360±16	350±17

rial. There is no significant influence of the structure of PVA mats electrospun using electrodes with tines (electrode types II and III). At a distance between electrodes of 15 cm and applied voltage of 65 kV, a denser mat is formed using a type I electrode (***Figure 4***). In all the electrospun mats presented (***Figures 3*** and ***4***), there are defects – spots of PVA solution. The shape of the electrode does not prevent defects in nonwoven PVA mats.

Figure 5 presents SEM images of TPU mats electrospun at a distance between electrodes of 17 cm and applied voltage of 65 kV. As was mentioned above, it was not possible to electrospin TPU solution using a plain cylindrical electrode (I). Only using electrodes with tines were porous mats electrospun from TPU solution. Contrary to the results obtained with PVA solution, there is a difference between TPU mats electrospun with electrodes II and III (***Figure 5***): The surface area of electrode II e is smaller and its tines are narrower than those of electrode III, which is why a thinner mat with a significantly lower amount of stick TPU fibres is formed using electrode II.

In this study two ways of calculating nanofibre diameter were chosen (***Table 2***): A* – all nanofibre derivatives from three SEM images were measured; B* – fibres with a diameter of up to 500 nm were eliminated from the calculation of the average nanofibre diameter, with the assumption that fibres with a diameter of up to 500 nm are stick nanofibres (during the electrosponning process, stick nanofibres should be eliminated from the calculation of the average nanofibre diameter). Analysing the average PVA nanofibre diameter (***Table 2***), we can state that the type of rotating electrode does not have an influence on the diameter of PVA nanofibres formed. From the histograms presented in ***Figure 6***, we can notice that with the applied voltage of 50 kV and the distance between the electrodes of 12 cm we formed 83% of PVA nanofibres with the diameter not exceeding 400 nm (0-400nm) using electrode type I, 73% of PVA nanofibres using electrode type II and 74% of PVA nanofibres using electrode type III. While increasing the distance to 15 cm (voltage 50 kV) we formed 83% of PVA nanofibres with the diameter not exceeding 400 nm using electrode type I, 74% using electrode type II and 70% using electrode type III.

Summing up, we can notice that it is possible to form PVA mats from thinner nanofibres using a cylindrical electrode.

From TPU solution porous mats were formed by the electrospinning process (***Figure 5***). There are a lot of stick TPU nanofibres in an electrospun mat formed by a type III electrode at an applied voltage of 65 kV and distance between electrodes of 17 cm. Then all derivatives of the electrospun fibres were measured from every SEM image, The average diameter of TPU nanofibres formed by a type III electrode is higher (***Table 2***) than for those formed by a type II electrode, due to the bigger amount of stick fibres. After the elimination of stick nanofibres (B*), the average TPU nanofibre diameter with type II and III electrodes is the same. Hence the type of electrode does not have an influence on the diameter of TPU nanofibres, only on the structure of the mats formed . Moreover, from the histogram presented in ***Figure 6d***, we can notice that there is only the tendency of the possibility of forming thinner TPU nanofibres using a type II electrode – 68% of all TPU nanofibres measured were within a diameter range of 200-500 nm, when a type II electrode was used, and 61% – when a type III electrode was used.

Conclusions

1. The electrospinning process depends on the type of polymer solution.
2. The type of bottom rotating electrode has an influence on the electrospinning process. In the case of an easily spun PVA polymer solution, a higher applied voltage is possible using an electrode with narrower tines (II).
3. Using all three types of bottom rotating electrodes is possible to electrospin mats from PVA nanofibres. Denser mats are formed using a plain cylindrical electrode due to its bigger surface area.
4. Using electrodes with tines of a higher electrostatic force is created nor using plain electrode, which is why nanofibres from less easily spun TPU solution are possible to form only using

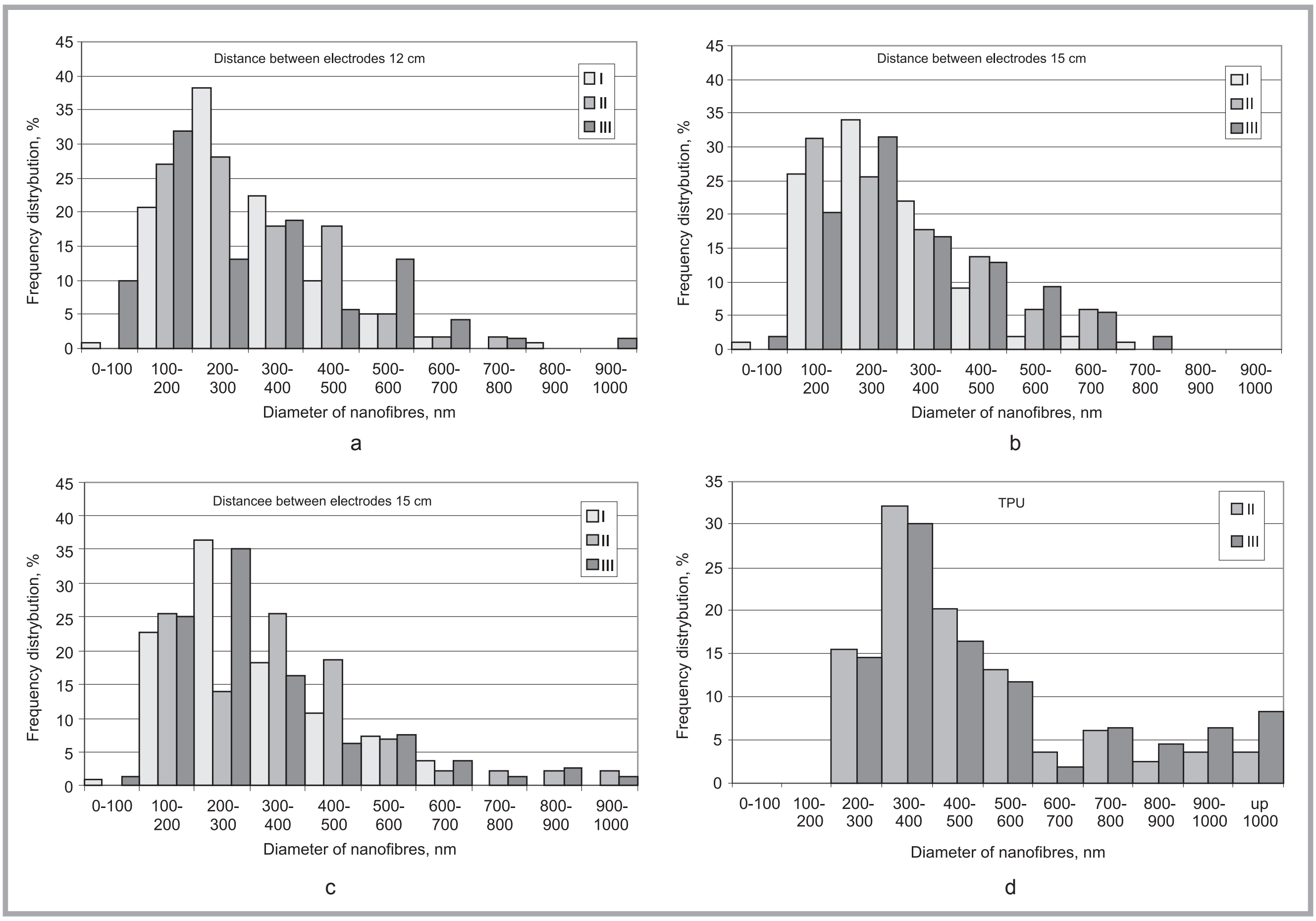

Figure 6. *Distribution of PVA nanofibres at a) an applied voltage (U) of 50 kV and distance between electrodes (L) of 12 cm, b) an applied voltage (U) of 50 kV and distance between (L) of 15 cm, c) an applied voltage (U) of 65 kV and distance between (L) of 15 cm; I – cylindrical electrode, II, III – electrodes with tines; d) Distribution of TPU nanofibres at an applied voltage (U) of 65 kV and distance between electrodes (L) of 17 cm, II, III – electrodes with tines.*

electrodes with tines. Mats with more stick TPU nanofibres are formed using electrode with tines, whose surface area is bigger (III).

5. The diameter of electrospun PVA or TPU nanofibres does not depend on the shape of the bottom rotating electrode, only the structure of formed mats depend from these electrodes.

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