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Formation of Electrospun PVA Mats on Different Types of Support Materials Using Various Kinds of Grounded Electrodes

Abstract

In this study nanofibres from poly(vinyl alcohol) (PVA) polymers solutions were collected on different types of support material by the electrospinning method (Nanospider™). During the electrospinning process, the following three different grounded electrodes were used: I - a cylindrical electrode II - a wire grounded electrode, III - a wire grounded electrode, whose distance to the support material was 40 mm. The aim of this research was to investigate the influence of the type of grounded electrode on electrospun PVA nanofibres collected on different support materials and their structure. During the experiments, it was noted that the type of grounded electrode has an influence on a electrospun mat with a PVA nanofibre structure. The diameter of electrospun PVA nanofibres does not depend significantly on the type of grounded electrode and nature of the support material, although it is possible to notice the tendency that it is possible to form a bigger amount of thinner nanofibres using type I grounded electrode.

Key words: electrospinning, nanofibre, PVA, support material.

Introduction

Electrospinning is a broadly used technology for electrostatic fibre formation which utilises electrical forces to produce polymer fibres with a diameter ranging from 2 nm to several micrometres using polymer solutions of natural or synthetic polymers. This process offers unique capabilities for producing novel natural nanofibres and fabrics with a controllable pore structure [1].

It is well known that the structure of electrospun mats depends on the polymer solution parameters (concentration, molecular weight, viscosity, surface tension, conductivity), processing parameters (applied voltage, flow rate, distance between electrodes), ambient parameters (humidity, temperature) and on the type of electrospinning apparatus [1, 3 - 7]. Cengiz et al. [3] explored and compared three different electrospinning methods: (A) a conventional spinning method with a single capillarity, B) Jirsak's electrospinning method and C) Yarin and Zussman's electrospinning method), their spinning possibilities, productivity and the influence of process parameters on PAN fibre properties. During this research, it was proved that the type of electrospinning apparatus has an influence on the structure of fibres. It was estimated that it was possible to form finer PAN fibres from a 10 wt% solution concentration by method C (Jarín & Zussman's method – nanofibres spun directly from the spinning solution surface) than by methods A (Conventional spinning method with the use of one capillar) or B (Jirsak's method - directly from the spinning solution) [3]. Research has also been done [4] on the in-

fluence of the shape of the spinning electrode (the electrode which is immersed in polymer solution) on the structure of the electrospun mat. During this research, conclusions were made that the type of bottom rotating electrode has an influence on the electrospinning process, and it was possible to form denser mats from PVA nanofibres using a plain cylindrical electrode instead of electrodes with tines; However, the diameter of the electrospun nanofibres did not depend on the shape of the bottom rotating electrode.

One more important aspect of the electrospinning process is the type of collector used. Nanofibres may be collected on a static collector or on dynamic collectors, for example rotating collectors. Collectors may be an aluminium or copper plate, a rotating drum, a disc collector, parallel electrodes, water, spunbond material etc. [4, 8, 9]. During researches on this, it was determined that the nature of the collector significantly influences the morphological and physical characteristics of the electrospun fibres. The density of fibres per unit area on the collector and

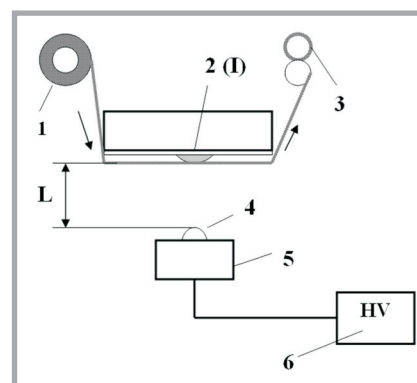


Figure 1. Principal scheme of electrospinning equipment – Nanospider™ (Elmarco): 1 - support material, 2 - grounded electrode (view from the front of the equipment), 3 - support material with a layer of nanofibres, 4 - bottom rotating electrode (plain cylinder), 5 - tray with polymer solution, 6 - power supply with positive polarity 0 - 75 kV; L - the distance between the bottom rotating electrode and support material is 130 mm.

the fibre arrangement are affected by the degree of charge dissipation upon fibre deposition [1, 2]. Liu et al. [10] electrospun cellulose acetate fibres on copper

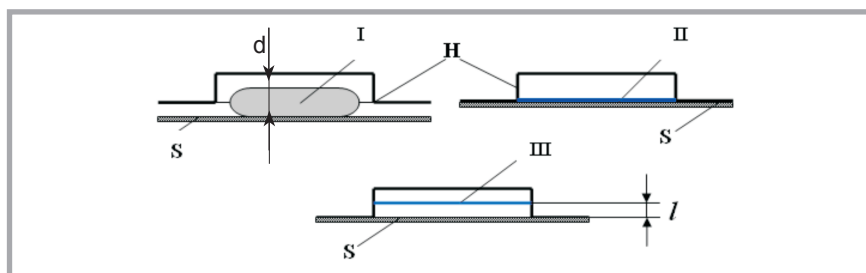


Figure 2. Principal scheme of grounded (fixed) electrodes (view from the side of the equipment): I - cylindrical electrode, diameter 70 mm, II, III - wire electrode, diameter - 0.5 mm, l - the distance between the support material and wire electrode is 40 mm, S - support material, H - frame of grounded electrodes.

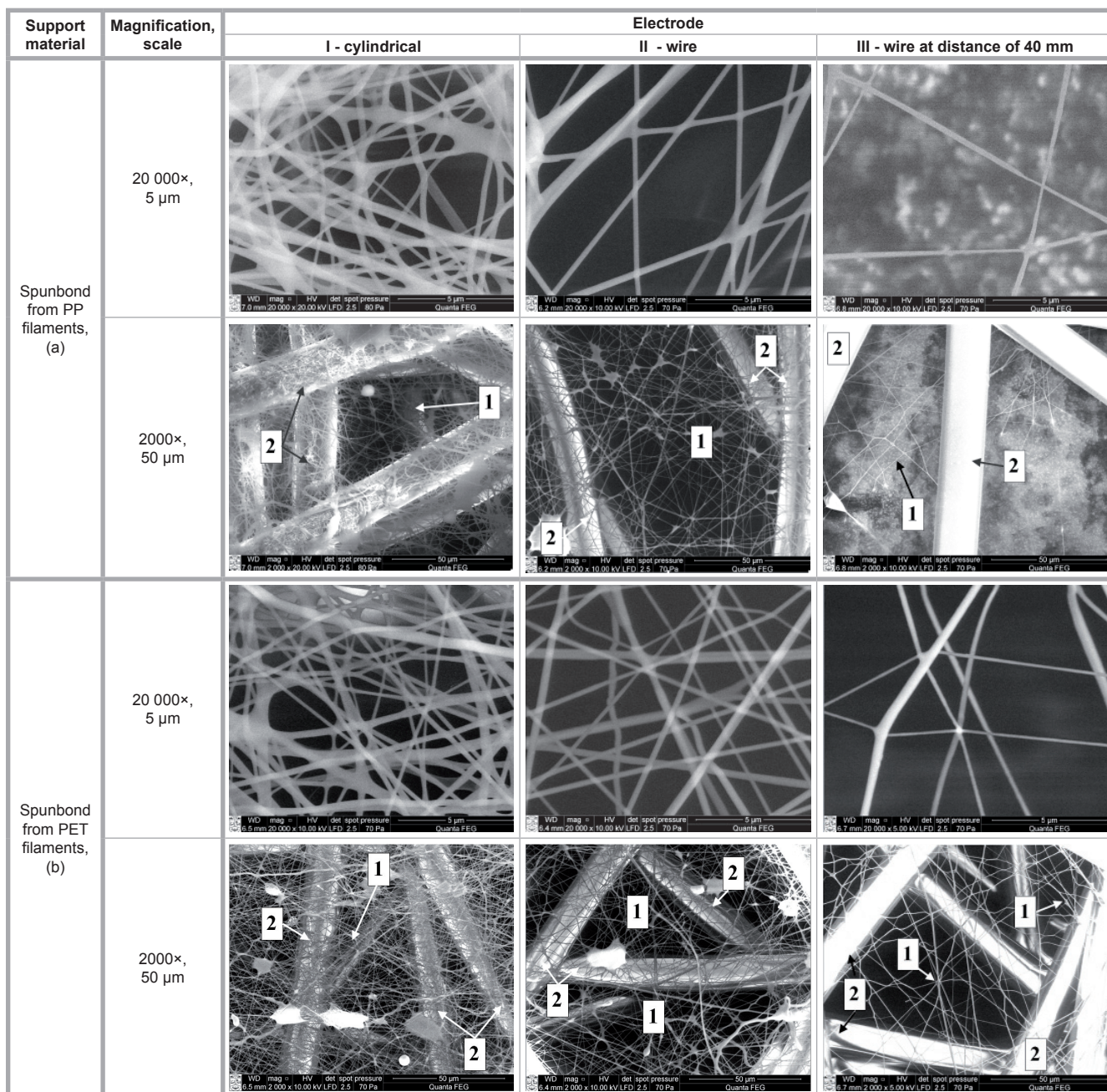


Figure 3. SEM images of electrospun PVA nanofibres during the first set of experiments (PVA spinning solution concentration - 8%), collected by 3 kinds of grounded electrodes (I – cylindrical, II - wire, III – wire at a distance of 40 mm from support material; on spunbonded support material of PP and PET filaments, a, b - designations in Figure 7, 1 - indicate nanofibres, 2 - fibres of support materials).

mesh, aluminum foil, paper and water. The nature of the collectors affected the fibre morphology and fibre packing. Fibres collected on paper had smooth surfaces, more uniform sizes and few defects. Fibres collected on water were more varied in size and more densely packed. Electrically conductive collectors such as aluminum foil and water favour a tightly packed and thick membrane structure, whereas a loosely packed fibrous network structure is formed on a nonconductive collector, like paper [10]. Kim et al. [11] electrospun PLLA and PLGA fibres on a metal plate and liquid. Using metal collectors, the surface of na-

nofibrous membranes was very smooth. When the metal collector was replaced by a water reservoir, the surface of the nanofibrous membranes became more rough [11]. Hakala and Heikkilä [12] collected nanofibres on press felts. It was estimated that mats of nanofibres improve the surface smoothness of press felts, at the same type reducing air permeability. In research using Jirsak's electrospinning (Nanospider™, Elmarco) method, nanofibres were mostly collected on spunbond from PP filaments [4, 5, 13, 14].

The aim of this study was to estimate the influence of the shape of a grounded

(fixed) electrode on the structure of electrospun PVA mats collected on different types and natures of support materials.

Materials

Powder of poly(vinyl alcohol) (PVA) (ROTH, Germany) $M = 72000$ g/mol. Support material spunbond from PP filaments $Q = 20$ g/m², spunbond from PET filaments $Q = 20$ g/m², aluminium foil, rib knit from PET fibres $Q = 300$ g/m², satin woven fabric from acetate fibres $Q = 140$ g/m², polyethylene film, and paper (100% cellulose).

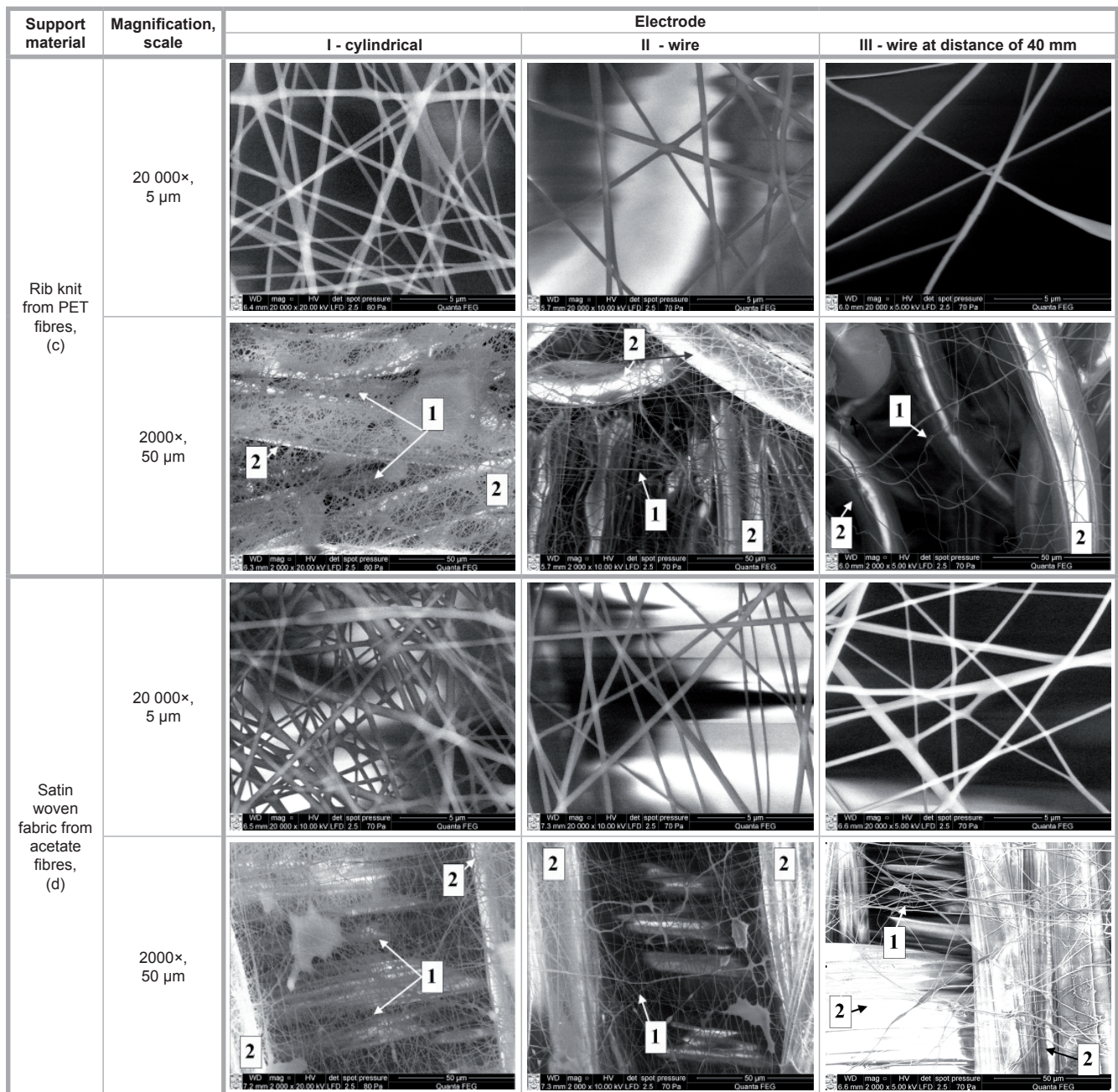


Figure 4. SEM images of electrospun PVA nanofibres during the *first set of experiments* (PVA spinning solution concentration - 8%), collected by 3 kinds of grounded electrodes (I – cylindrical, II - wire, III – wire at a distance of 40 mm from support material; *on support material of rib knit from PET fibres and satin woven fabric from acetate fibres, c, d - designations in Figure 7, 1 - indicate nanofibres, 2 - fibres of support materials.*

■ Methods

Preparation of polymers solutions

PVA solution was prepared by dissolving PVA powder for 2 hours at 70 °C in distilled water by magnetic stirring.

Electrospinning equipment

The substratum materials were covered by a layer of PVA nanofibres using a “Nanospider™” (Elmarco, Czech Republic) (Figure 1, see page 34).

In this study two types of fixed grounded electrodes were used: I – a cylindrical

electrode with a diameter of 70 mm and length of 210 mm, and II & III – wire electrodes, diameter – 0.5 mm, length - 345 mm; in the case of types I and II the support material touched them, and for type III the distance between the support material and fixed electrode was 40 mm (Figure 2, see page 34).

A mat from PVA nanofibres was formed at an applied voltage of 60 kV and distance between the electrodes of 13 cm; the temperature of the electrospinning environment was $t = 18 \pm 2$ °C and the air humidity $\gamma = 45 \pm 2\%$.

To analyse the influence of the type of grounded electrode on the electrospinning process, two sets of experiments were performed:

1) from every type of support material samples were cut of 15 cm × 15 cm size, which were attached to the main support material – conductive spunbond from PP filaments $Q = 20$ g/m², i.e. nanofibres were collected on different types of support materials (spunbond from PP filaments $Q = 20$ g/m², spunbond from PET filaments $Q = 20$ g/m², satin woven fabric from acetate fibres $Q = 140$ g/m², rib knit from PET fibres $Q = 300$ g/m², poly-

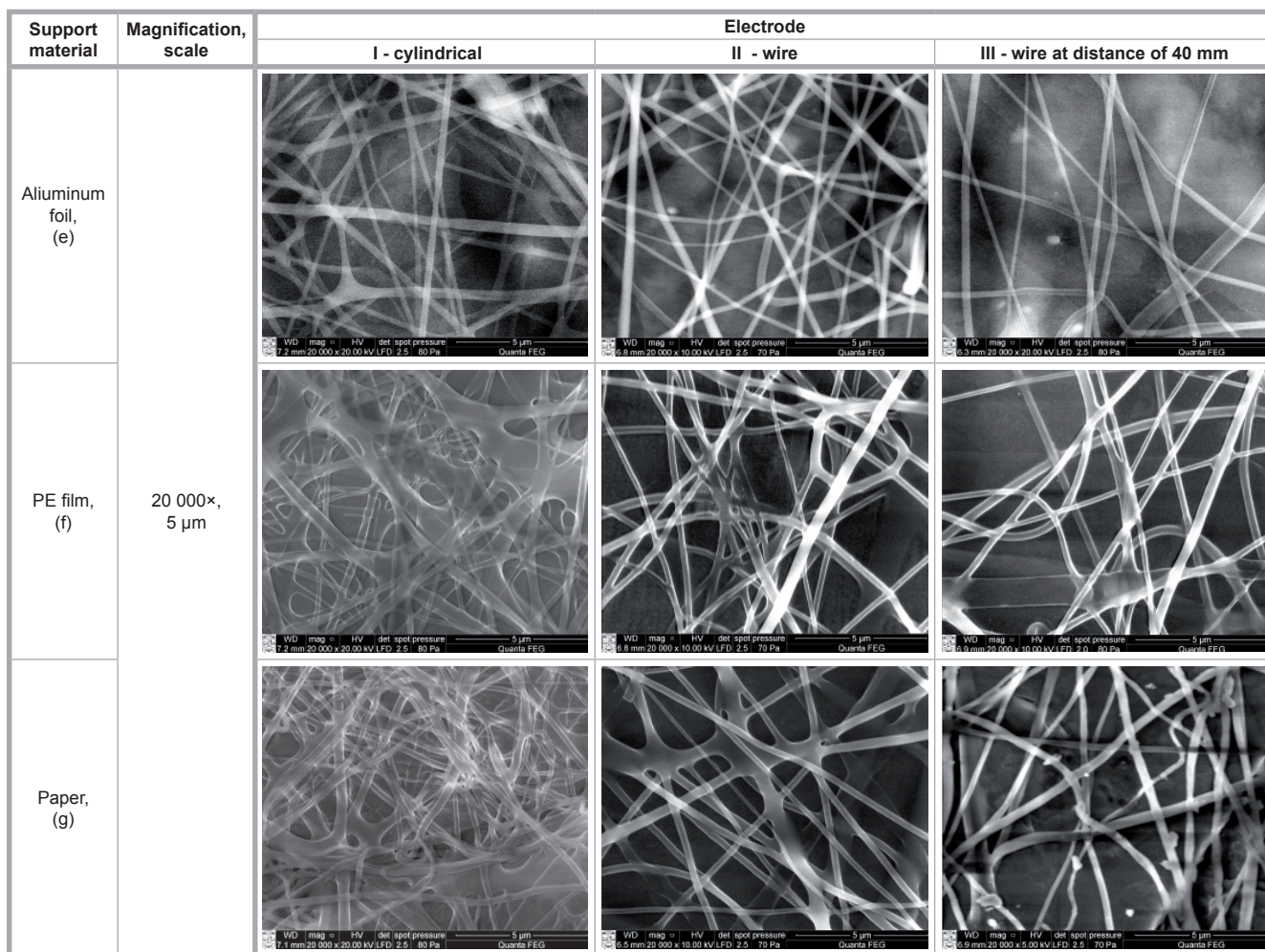


Figure 5. SEM images of electrospun PVA nanofibres during the first set of experiments (PVA spinning solution concentration - 8%), collected by 3 kinds of grounded electrodes (I – cylindrical, II - wire, III – wire at a distance of 40 mm from the support material; on support material of aluminum foil, PE film and paper, e, f, g - designations in Figure 7.

ethylene film, aluminium foil and paper (100% cellulose);

2) nanofibres were collected on support materials spunbond from PP filaments $Q = 20 \text{ g/m}^2$, spunbond from PET filaments $Q = 20 \text{ g/m}^2$ and satin woven fabric from acetate fibres $Q = 140 \text{ g/m}^2$, with a width of 40 cm, i.e. the support material covered all the grounded electrode.

Characterisation techniques

The structure of the PVA nanofibres mats was determined using a scanning electron microscope - (SEM) Quanta - 2000 (FEI). The diameter of PVA nanofibres was measured using an image analysis system - LUCIA 5.0. All derivatives of the nanofibres (single, stick) from every SEM image were measured.

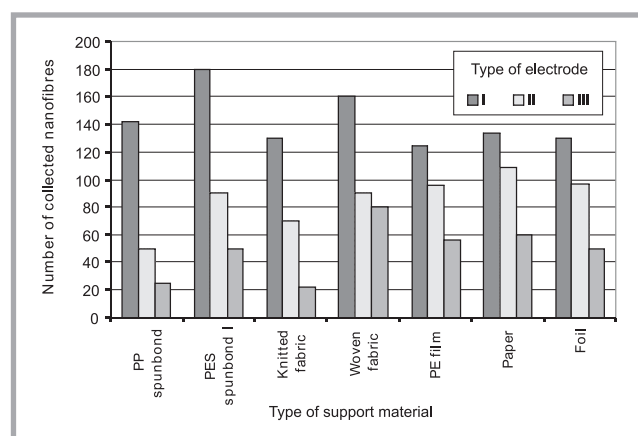
Results and discussion

In electrospinning, the polymer solutions are charged while travelling toward the collector. Whether or how the residual charge is dissipated affects how fibres

repeat each other and the fibre arrangement. Jets of polymer solution reaching the collector still contain solvents, and the nature of the collector affects the diffusion and evaporation of the residual solvent from the fibres, which may influence the fibre structure [10]. The strength and uniformity of the electric field created depend on the diameter of the grounded electrode. In order to es-

timate the influence of the shape of the grounded electrode on the electrospinning process and structure of the electrospun mat, the influence of the nature of the support material on the possibility of covering it by a layer of nanofibres was also estimated. Different types and natures of support materials, as specified in the last chapter, were chosen. During the electrospinning process, nanofibres are

Figure 6. Dependence of the number of collected PVA nanofibres (number of nanofibres from three SEM images at a scale of 5 μm) on different support materials from grounded electrodes types I, II and III.



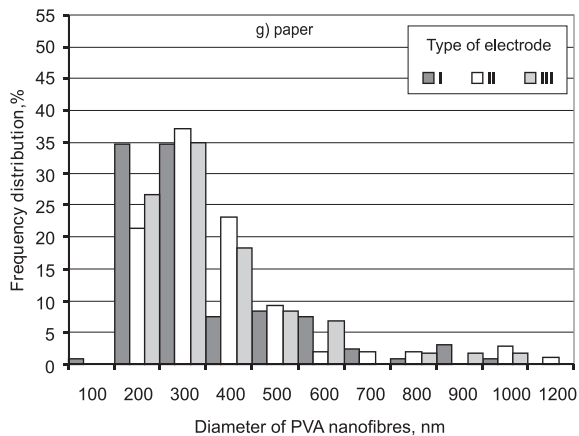
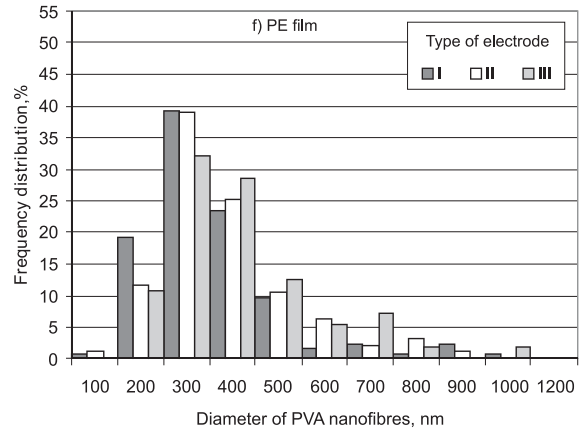
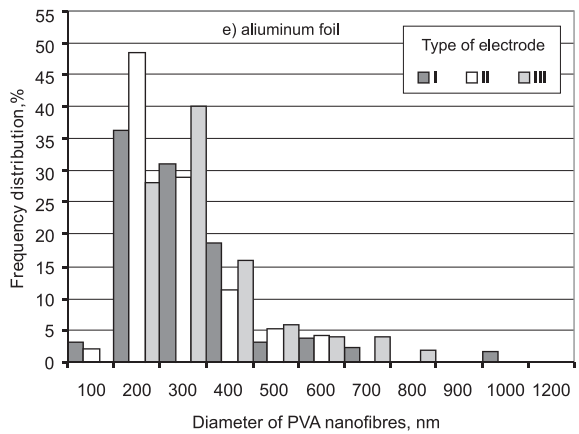
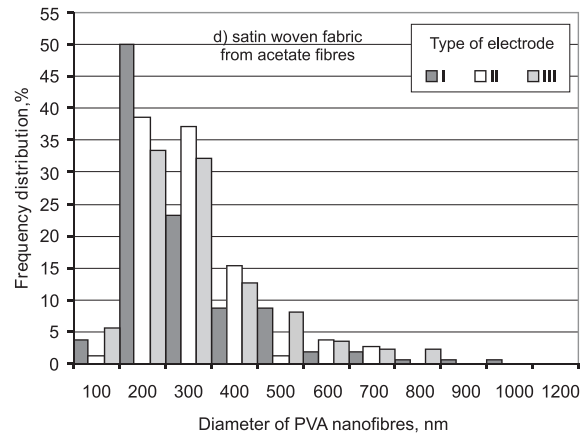
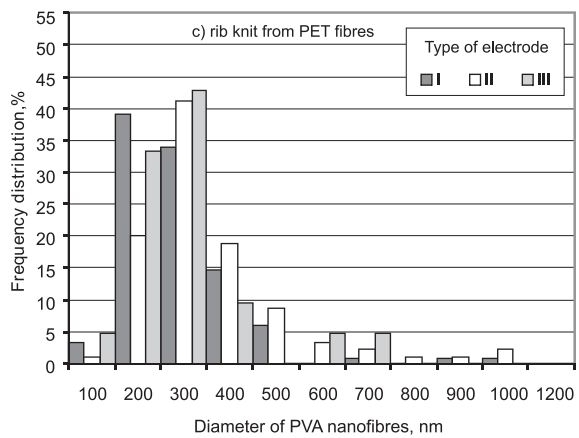
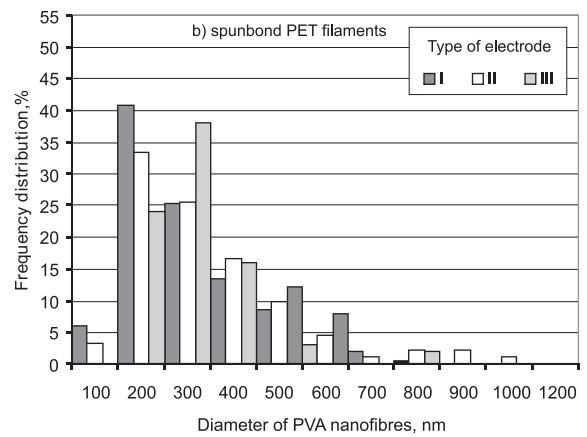
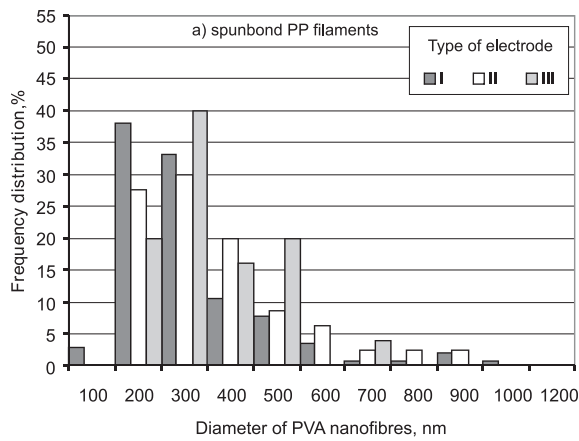


Figure 7. Distribution of PVA nanofibres collected on support materials (150 mm × 150 mm); a) PP spunbond b) PET spunbond, c) rib knit from PET fibres, d) satin woven fabric from acetate fibres, e) aluminum foil, f) PE film and g) paper.

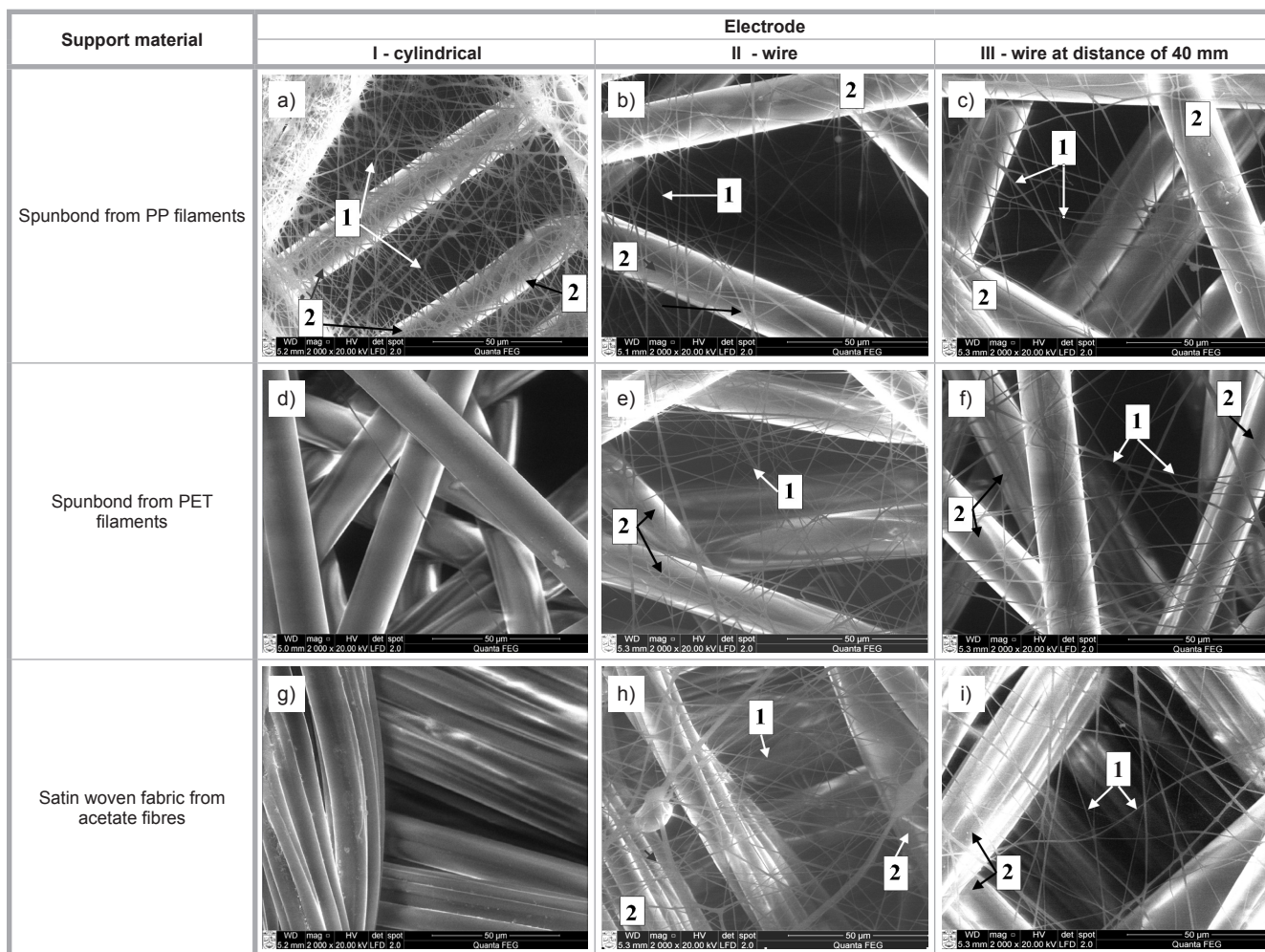


Figure 8. SEM images of electrospun PVA nanofibres during the second swet of experiments (PVA spinning solution concentration 10%) collected by 3 kinds of grounded electrodes (I –cylindrical, II – wire, III –wire at a distance of 40 mm); on support material of nonwoven from PP & PET filaments and satin woven fabric from acetate fibres.

collected on the moving support material. Such materials as paper and foil are quite weak, and during stretching they can tear. Therefore squares of the support materials were cut and attached to conductive spunbond from PP filaments. The first part of the research showed that by using different types of grounded electrodes, it is possible to cover all kinds of support materials by a layer of nanofibres if they are attached to a conductive material (in this test, to spunbond from PP filaments) (Figure 3, see page 35).

Table 1 presents the parameters of the electrospinning process using different types of grounded electrodes, and a distance between bottom electrode and support material of 130 mm and 170 mm. From the results presented is possible to notice, that the type of grounded electrode has influence on the electrospinning process. When the distance between bottom electrode and support material (L) is 130 mm, applied voltage 55 kV or 60 kV, the values of current are significantly

lower using, the wire electrode II then the cylindrical (I) one, i.e. the strength of the electric field is lower. A weaker electrical field is also created with an increase in the distance between support material and grounded electrode (compare II type with III type of electrodes). It can be also seen, that at $L = 170$ mm, $U = 55$ kV or 60 kV, III electrode using, it was not possible to form nanofibres due to the high distance (170 + 40) mm between the bottom and the grounded electrodes.

After initial tests carried out we accepted 60 kV and $L = 130$ mm for all tests

presented in this article by SEM and bar charts.

From the SEM images presented in Figures 3, 4 & 5 (see pages 35, 36 & 37), it can be seen that the type of fixed electrode has an influence on the structure of electrospun PVA material. Thicker nonwoven materials with more spots of polymer solution were formed on all the kinds of support materials using electrode I. The biggest amount of collected nanofibres occurs for type I electrode (Figure 6, see page 37). As was mentioned, the electric field is higher for type I electrode, due

Table 1. Parameters of the electrospinning process using different types of grounded electrodes.

Polymer solution	Distance between electrode and support material (L), mm	Applied voltage (U), kV	Current (I), mA		
			I fixed electrode	II fixed electrode	III fixed electrode
PVA	130	55	0.110 - 0.140	0.040 - 0.080	0.005 - 0.060
		60	0.180 - 0.200	0.060 - 0.120	0.040 - 0.090
	170	55	0.030 - 0.060	0.014 - 0.035	-
		60	0.080 - 0.100	0.035 - 0.055	-
		70	-	-	0.003 - 0.030

Table 2. Average diameter of electrospun PVA nanofibres (concentration of solution - 8%) collected on different types of support materials; A* - all fibres visible in the SEM image were measured, and on this basis the average fibre diameter was calculated, B* - fibres of diameter above 500 nm were eliminated from the average value calculation, as fibres formed from two or three fibres glued together.

Type of support material (150 mm × 150 mm)	Fibre diameter, nm - spun on electrodes					
	electrode					
	I - cylindrical		II - wire		III - wire at distance of 40 mm	
	A*	B*	A*	B*	A*	B*
PP filaments (a)	265 ± 32	230 ± 20	310 ± 39	257 ± 24	300 ± 52	286 ± 42
PET filaments (b)	250 ± 26	230 ± 20	290 ± 37	248 ± 22	302 ± 40	272 ± 30
Rib knit (c)	250 ± 26	232 ± 18	310 ± 39	270 ± 22	260 ± 66	220 ± 36
Satin woven fabric (d)	240 ± 28	217 ± 20	244 ± 26	221 ± 19	274 ± 30	243 ± 21
Aluminium foil (e)	270 ± 30	235 ± 18	240 ± 21	223 ± 16	290 ± 39	250 ± 23
PE film (f)	310 ± 32	272 ± 18	333 ± 30	290 ± 16	360 ± 46	302 ± 24
Paper (g)	300 ± 36	240 ± 18	322 ± 40	270 ± 35	306 ± 45	260 ± 25

to which more Taylor cones are formed on the rotating cylindrical electrode, and consequently more nanofibres cover the support material. From the SEM images presented in **Figure 3, 4 & 5** (see pages 35, 36 & 37), it can be noticed that the nature of the support material also has an influence on the structure of electrospun mats - they are more stick, not separated nanofibres in the mats collected on PE film and paper.

In this study two ways of calculating the nanofibre diameter were chosen (**Table 2**): A* - all nanofibre derivatives were measured from three SEM images; B* - from the calculation of the average nanofibre diameter, fibres with a diameter over 500 nm were eliminated [4]. By analysing the nanofibre diameter for different support materials, it can be seen that by using the type I of electrode, the average diameter of PVA nanofibres is mostly smaller than when using the type II electrode, but this difference is of minor significance. **Figure 7** (see page 38) presents the distribution of the diameter of PVA nanofibres collected on different types of support material of 150 mm × 150 mm size. From the histograms presented, we can notice the tendency that by using a type I electrode, more thinner nanofibres are formed (fibres with a diameter of up to 200 nm). For PET spunbond support material using a I type electrode, 47% of nanofibres had a diameter of up to 200 nm, for II type it was 37% and for type III - 24%; consequently, for woven fabric, using I - 54%, II -40%, and III -39%, for knitted fabric I- 43%, II-21%, and III - 37%, for PE film I-20%, II-12%, and III-11%, for paper I- 36%, II -21%, and III-27%, for spunbond from PP filaments I- 41%, II -28%, and III-20% of PVA nanofibres were measured as having a diameter up to 200 nm. However, for aluminium foil, a bigger amount of na-

nofibres with a diameter of up to 200 nm were measured using a type II grounded electrode - 51%, while for type I it was 40% and III - 28%. Aluminum foil has the highest conductivity of all the other support materials and this is the reason of the results obtained, as earlier assumed.

During the second set of experiments, three types of support materials were chosen: spunbond from PP fibres, $Q = 20 \text{ g/m}^2$, spunbond from PET fibres, $Q = 20 \text{ g/m}^2$ and satin woven fabric from acetate fibres, $Q = 140 \text{ g/m}^2$. In this case the width of the materials was 40 cm, i.e. the whole length of the grounded electrode was covered by the support material. When analysing the electrospun samples, it was noticed that when using a type I electrode, only PP spunbond was covered by a layer of nanofibres (**Figure 8**, see page 39). It was possible to partially cover woven fabric and spunbond from PET fibres using only type II and III electrodes. Such results are influenced by a change in the electric field. The strength and uniformity of the electric field depends on the diameter of the grounded electrode. By using an electrode with a bigger diameter, a more uniform electric field is created.

From the SEM images presented, it is possible to notice that a thicker layer of nanofibres was formed using electrode I (**Figure 8.a - 8.c**, see page 39). From the second set of experiments it was also determined that the type of grounded electrode does not have a significant influence on the diameter of electrospun PVA nanofibres on support material spunbond from PP filaments.

Conclusion

1. The structure of electrospun mats depends on the type of grounded electrode. Electrospun mats formed by

using thinner grounded electrodes are evidently sparsely structured.

- The type of grounded electrode does not have a significant influence on the diameter of electrospun nanofibres. There is a visible tendency that a bigger amount of thinner nanofibres is possible to form using type I grounded electrode.
- Analysing the influence of the type of grounded electrode on the possibility of covering support materials of a different nature by a layer of nanofibres, we can conclude that if different support materials (textiles, films) are attached to a conductive support, it is possible to cover it using all three types of grounded electrodes. By using a thinner grounded electrode, we have the possibility to cover different types and natures of support materials with a layer of nanofibres which would cover all the length of the grounded electrode.

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