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Formation of Thermoplastic Polyurethane (TPU) Nano/Micro Fibers by Electrospinning Process Using Electrode with Tines

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Electrospinning is a process during which polymer fibers with a diameter in nano and micro range due to the action of an external electric field effected on a polymer solution or melt are produced. The aim of this study is to form thermoplastic polyurethane (TPU) mats by electrospinning process. TPU solutions of 3 wt.% and 4 wt.% concentrations were prepared for the experiments. It was not possible during the tests to create any TPU fibers using plain cylindrical electrode, so two types of electrodes with tines were used in this study. TPU mats from microfibers, nanofibers and stick nanofibers were formed by electrospinning process at different applied voltage and solution concentrations. It was determined that the type of electrode has influence only on the structure of the electrospun TPU mats, but not on the diameter of formed fibers.

Keywords: nanofiber, electrospinning, thermoplastic polyurethane.

INTRODUCTION

Electrospinning is a process that employs electrostatic forces to produce nanofibres with a diameter between 10 nm – 500 nm and microfibres with a diameter between 0.5 μm – 1 μm from polymer solutions or melt [1]. More than 50 polymers have been successfully spun into fibres through this technique [2]. Electrospinning is an old technique. It was first observed in 1897 by Rayleigh, studied in detail by Zeleny (1914) on electrospraying, and patented by Formhals in 1934. The work of Taylor (1969) on electrically driven jets has laid the groundwork for electrospinning [3].

Electrospun mats from polymer fibres are drawing a great attention because of their unique properties such as high surface-to-volume ratio, high porosity, small diameters, flexibility in surface functionalities and superior mechanical performance. Many parameters have influence on the transformation of polymer solution into nanofibres: viscosity (concentration), conductivity, elasticity, temperature, surface tension of the solution, polymer molecular weight, applied voltage, distance between electrodes, humidity and air velocity in the electrospinning chamber [4, 5]. Nonwoven materials from nanofiber and microfibers have many potential uses as barrier membranes against micro-organisms, filter media for submicron dust, and other potential uses appropriate to their strength, surface energy, wettability, dyeability etc. [6, 7]. The electrospun nanofibers can be used to construct unique functional nanostructures. Especially, high surface area of electrospun mat can provide reactive sites for chemicals or biocides so that it would make a very good candidate for biomaterial or chemical protective clothing. Additionally, nano or micro-pores of the electrospun mat provides good moisture and vapor release properties, while it maintains water and wind resistance, so that it can be well applicable to waterproof-breathable fabrics. High thermal insulation resulting from large volume of air in microscopic pores would be another advantage. Other application can also be found in sensors, reinforced composites, drug delivery materials and special textiles [1].

Polyurethane (PU) is a polymer in which individual units in the main chain of macromolecule's is connected by urethanes groups [8]. PU can be used in medicine tissue engineering (ligament reconstruction), wound dressing, drug/gene delivery, to cover medical devices, materials for sanitation and health care [3, 8, 9]. Among PUs, there is one group of very promising smart materials called shape-memory PU. They can change their shape, hydro absorbency, water vapor permeability, stable of water, self-cleaning ability, optical and other properties when external change. Also PU can be used for production in high-efficiency filters, protective textiles, sensors, food packaging, and biosensors [8, 9 – 12]. Thermoplastic polyurethane (TPU) is used in medicine for good compatibility with blood, also it can be used as heart valves, ventricular frame. TPU presents a class of polymers that possess a range of very desirable properties: they are elastomeric, resistant to microorganisms and abrasion and have excellent hydrolytic stability [13]. TPU can be dissolved in tetraetilamoniumbromide, N,N-dimethylformamide, dimethylacetamide, ethanol, tetrahydrofuran, and mixtures thereof [11, 14]. TPU viscous state is achieved by heating it to about 120 °C temperature [1].

Y. K. Kang with co-authors determined mat of electrospun PU (Hyosung Manufacturing R&D Center) are excellent candidates for breathable water-proof fabrics. It was defined that electrospun PU mat had lower weight for the same thickness and surface area. Electrospun mat applied fabric had superior air permeability and moisture transport properties compared with resin coated fabrics. Also electrospun PU mat showed the highest thermal insulation among the specimens tested, due to the micro pores of the web holding large amounts of air [1].

O. Jirsak with co-authors investigated the effect of tatraethylammoniumbromide (TEAB) salt on the spinnability of PU (Larithane LS 1086) nanofibers via roller elctrospinning method. They determined, that TEAB

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salt concentration has an important effect on the conductivity, viscosity, spinning performance, fiber diameter and fiber morphology. They found that PU having 1.82 % TEAB gives the best result about spinning performance. However when they considered the other fiber properties such as diameter, uniformity and morphology, the optimum value is the 0.87 % TEAB to obtain ideal PU nano structure [14].

J. E. Sanders with co-authors have analyzed the polyurethane (PU) (Estane 58315, BF Goodrich, Cleveland, OH), polyester (PES), polyethylene (PET) and poly(L-lactic acid) (PLA) electrospun microfibers diameter. During this study it was estimated that the percentage of fibers with diameter 1 μm – 5 μm was greater for PET and PU (75.0 % and 71.4 % respectively) than for PE and PLA (45.5 % and 56.3 % respectively) [15].

D. Cha with co-authors researched the dependence of shape-memory PU block copolymers fibers diameter upon solution concentration and viscosity. It was stated that the PU fibres electospun from lower viscosity (ca. 130 cPs – 180 cPs) had diameter about 800 nm and a beaded-on-fiber structure. In contrast, the samples spun at a higher PU solution viscosity (ca. 530 cPs – 570 cPs) showed a smooth fiber surface with an average diameter about 1300 nm. The electrospun PU nonwovens with a hard-segment concentration of 50 wt.% had higher stress than those with a hard-segment concentration of 40 wt.% [16].

M. M. Demir with co-authors have studied that PU (based on poly(tetramethylene oxide) glycol, a cycloaliphatic diisocyanate and an unsymmetrical diamine fiber diameter increase as the third power of solution concentration. Low concentration solutions drive towards the formation of fibers with beads, whereas increased concentration favors the formation of curly PU fibers [17].

The aim of this study is to form thermoplastic polyurethane mats by electrospinning process using different types of electrode at different applied voltage and solution concentrations. Electrode with tines and different solution concentration were tested to study influence on an average diameter of the electrospun fibers.

MATERIALS AND METHODS

TPU fibers were electrospun by Nanospider^{TM} (Elmarco, Czechia) (Fig. 1). Roller electrospinning method with high voltage power supply was used to spin fibers. Nanospider consists of rotating electrode to spin fibers directly from the polymer solution. The TPU polymer solution is filled into a tray and the bottom rotating electrode is partially immersed into the polymer solution. High voltage is connected to the rotating roller. The collector electrode is usually grounded to create potential difference. Many Taylor cones are created as the cylinder rotates along the top part of the roller. As the solvent evaporates, the jets of polymer solutions are transformed and the solid fibers are obtained before reaching to the collector electrode [14].

Electrodes with tines were chosen in this study, because to create TPU fibers by electrospinning process using plain cylindrical electrode was impossible. Using cylindrical electrode the enough strong electric field is not formed, by means of which the continuous flow of Taylor cones would form. While using electrode with tines, according electric field theory the major supply of electric charge were collected on the top of tines, where the surface curvature is greater and surface electric field density in these places is higher. Consequently the continuous flow of Taylor cones on the tines was formed.

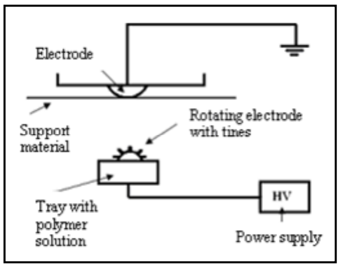
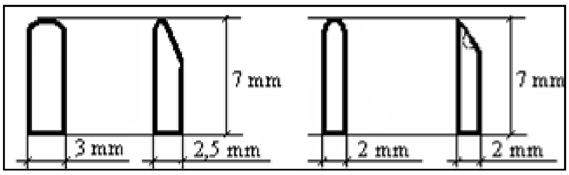


Fig. 1. The scheme of "Nanospider"

Two types of electrodes were used for the electrospinning process – I type electrode and II type electrode (Fig. 2, a and b). The electrode consists of eight separate plates. In every plate tines are set at equal distances. Tines are different by the width and shape of every electrode. Tines of II type electrode have grooves.



a b

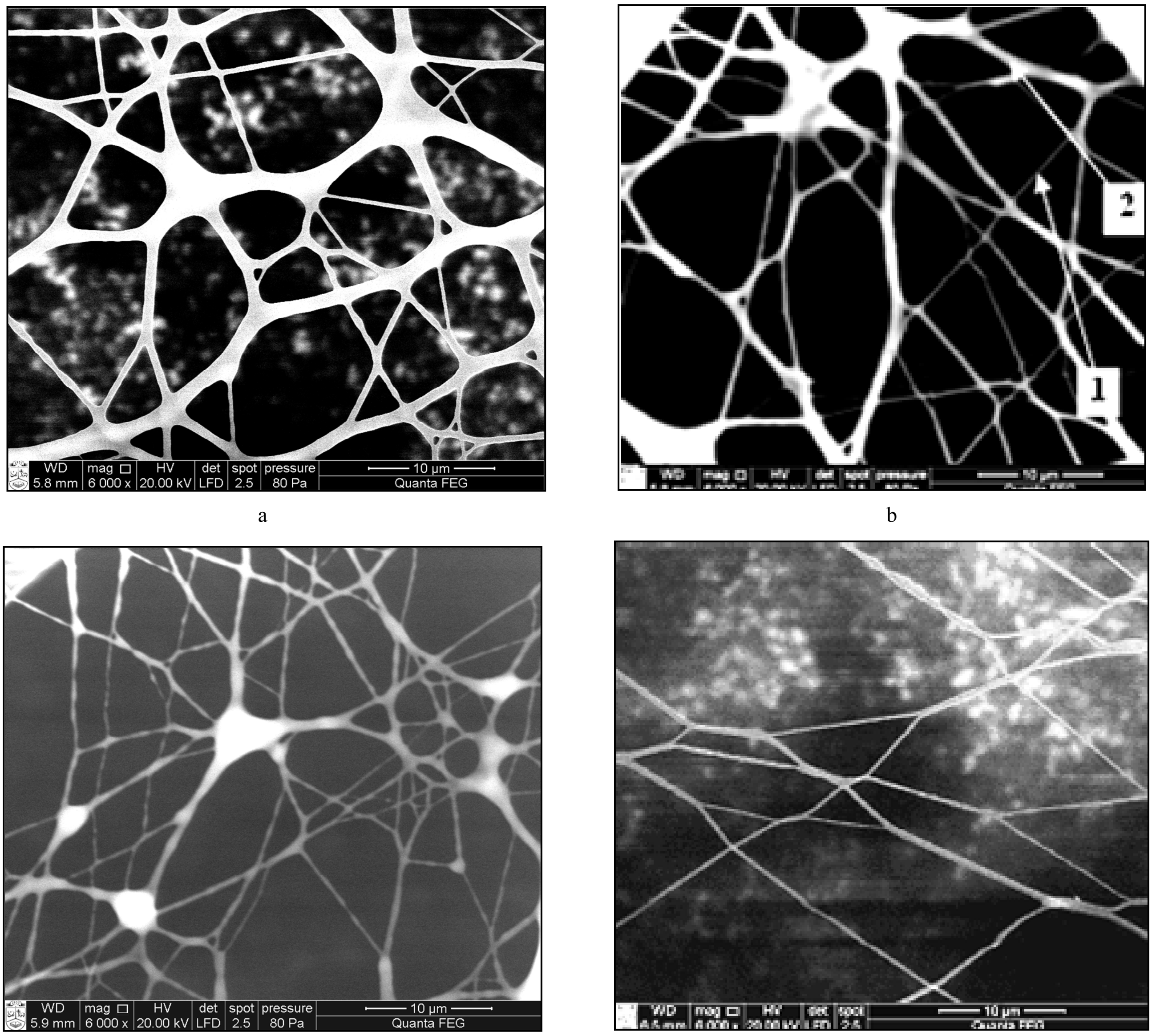
Fig. 2. Tine of electrode: a – tine of I type of electrode; b – tine of II type of electrode

Thermoplastic polyurethane (TPU) (Laripur, Coim Group, Italy) solution was prepared by dissolving TPU granules in a mixed of dimethylformamide (DMF) and tetrahydrofuran (THF) (DMF : THF = 1 : 1, w/w) solvent. The solution was mixed for 48 hours. TPU solutions of 3 wt.% and 4 wt.% concentrations were prepared for the test. The distance between Nanospider^{TM} electrodes was 17 cm. The applied voltage was 55 kV and 65 kV. Temperature of the electrospinning environment $T = 20\,°C \pm 2\,°C$, air humidity $\varphi = 40\,\% \pm 2\,\%$.

The structure of electrospun mats was determined using scanning electron microscope (SEM) Quanta 2000 (FEI). The diameter of electrospun TPU fibers were measured with software LUCIA 5. Measurements of the diameter of electrospun fibers were chosen at random, excluding derivatives of nanofibers. All fibers (single and stick) were measured from every SEM images, the average diameter of all fibers and average diameter of fibers to 500 nm was calculated.

RESULTS AND DISCUSSION

TPU mat was formed from fibers of different diameters, therefore the average diameter of fibers was calculated. In Fig. 3 SEM images of electrospun TPU mats, when used I type electrode (a, c) and II type electrode (b, d) was used, are presented. Concentration of solution a, b – $C = 4$ wt.% and c, d – $C = 3$ wt.%, applied voltage (U) was 65 kV.



a b

c d

Fig. 3. SEM images of electrospun TPU mats at 65 kV applied voltage, $C = 4$ wt.% (a, b), $C = 3$ wt.% (c, d): a, c – TPU mats then was used I type electrode; b, d – TPU mats obtained using II type electrode; 1 – indicate fibers, 2 – derivative of fibres (stick fibres)

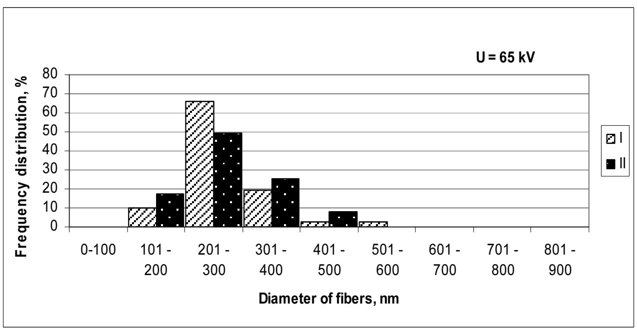


Fig. 4. The distribution of TPU fibers diameter at 65 kV applied voltage, $C = 3$ wt.%: I type of electrode; II type of electrode

Analyzing SEM images in Fig. 3, a, b, ($C = 4$ wt.%) we can see, that electrospun porous mat was formed from fibers which diameters vary in the range $d_{\mathrm{Imin}} = 190$ nm up to $d_{\mathrm{Imax}} = 1110$ nm. The average of fibers diameter wasn't calculated in this case, because the mat was formed of the derivatives of stick fibers, whose formation are influenced by the solution concentration.

When concentration of TPU solution is $C = 3$ wt.% (Fig. 3, c), electrospun mat consists of plenty stick or not split fibers. The average diameter of fibers, when I electrode was used, is $\bar{d}_{\mathrm{I}} = 270$ nm ±30 nm and with II electrode $\bar{d}_{\mathrm{II}} = 275$ nm ±30 nm. The assumption was made that fibers with the diameter higher than 500 nm are stick nanofibers.

The average diameter of TPU fibers after elimination fibers thicker than 500 nm is $\bar{d}_{\mathrm{I\ to\ 500}} = 265$ nm ±25 nm, $\bar{d}_{\mathrm{II\ to\ 500}} = 275$ nm ±30 nm. These results show that the type of electrode does not have significant influence on diameter of electrospun fibers.

Analyzing the distribution of TPU fibers diameter (Fig. 4) it is possible to state, that the type of electrode does not have significant influence on formed nanofibers diameter, because 2 % difference is too small to claim that the type of electrode has influence on the diameter of TPU fibers (98 % fibres with diameter 0 nm – 500 nm were

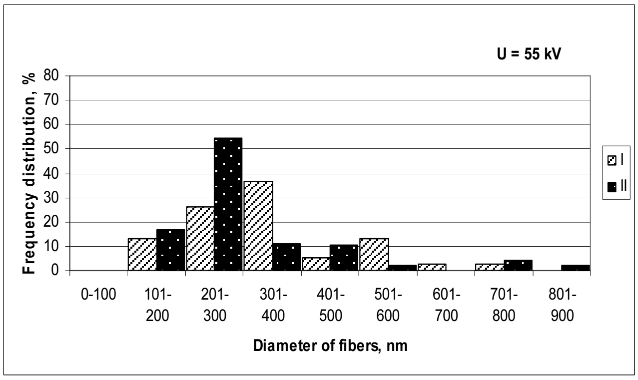


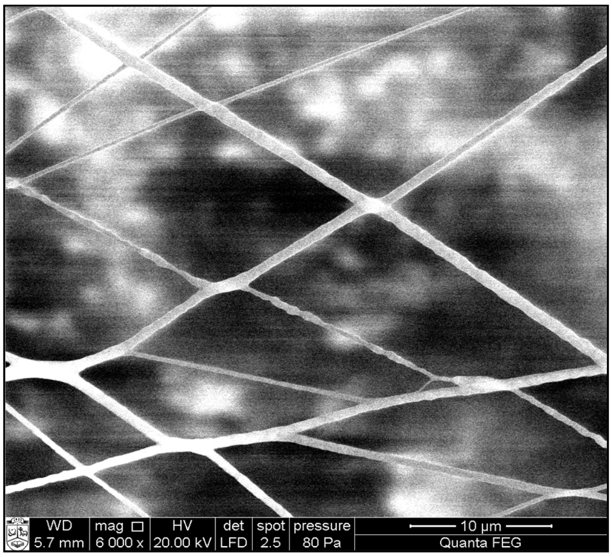
Fig. 5. The distribution of TPU fibers diameter at 55 kV applied voltage, $C = 4$ wt.%: I type of electrode; II type of electrode

measured, when I type electrode was used, and 100 % – II type electrode). 15 % thinner nanofibers more formed in the range 201 nm – 300 nm when using I type electrode.

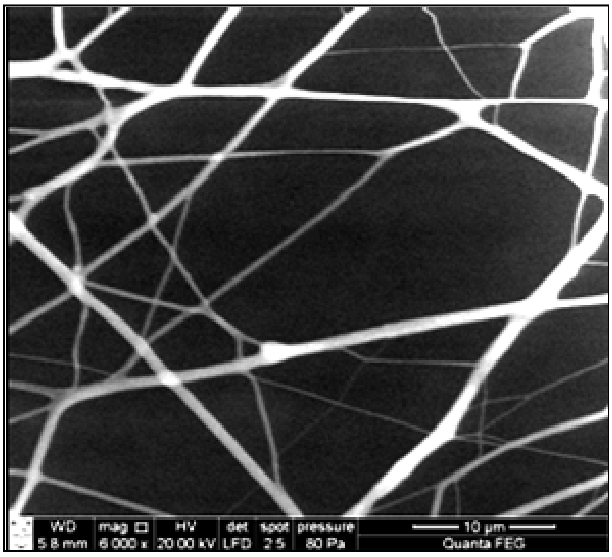
Analyzing the distribution of TPU fibers diameter ($C = 4$ wt.%) (Fig. 5) it is possible to state, that 81 % fibres with diameter 0 nm – 500 nm were measured (I type electrode were used), and 92 % fibers with the diameter 0 nm – 500 nm were measured using II type electrodes. 55 % nanofibers formed in the range 201 nm – 300 nm when using II type electrode.

In Fig. 6 SEM images present electrospun TPU mat when I type electrode (Fig. 6, a, c) and II type electrode (Fig. 6, b, d) were used: $U = 55$ kV, $C = 4$ wt.% (Fig. 6, a, b) and $C = 3$ wt. % (Fig. 6, c, d).

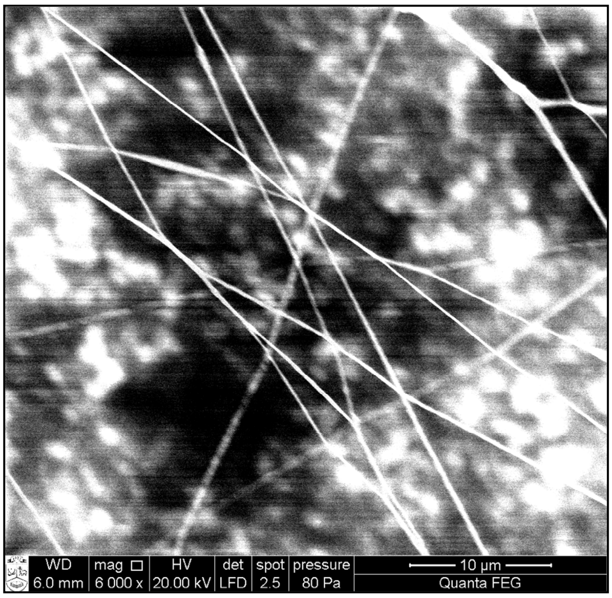
From SEM images it is possible to notice that in all cases mat from single nanofibres and stick nanofibres was elecrospun. The average diameter of electrospun TPU



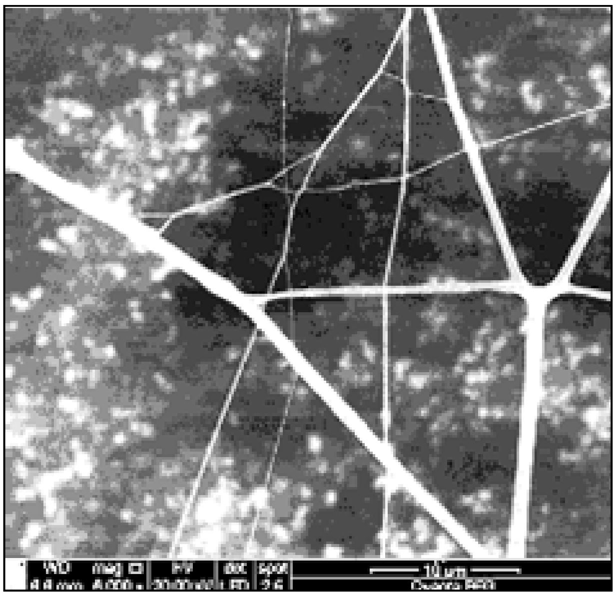
a



b



c



d

Fig. 6. SEM images of electrospun TPU mats at applied voltage 55 kV, $C = 4$ wt.% (a, b), $C = 3$ wt.% (c, d): a, c – electrospun TPU mat then was used I type electrode; b, d – electrospun TPU mat then was used II type electrode

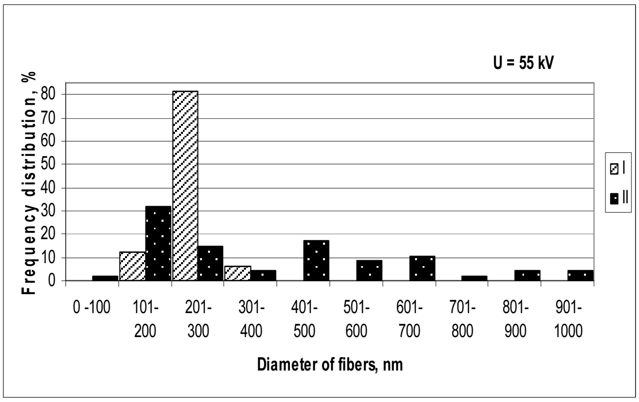


Fig. 7. The distribution of TPU fibers diameter at 55 kV applied voltage, C = 3 wt. %: I type electrode; II type electrode

fibers (Fig. 6, a, b) is $\bar{d}_{I}$ = 350 nm ±65 nm and $\bar{d}_{II}$ = 305 nm ±60 nm then U = 55 kV, $C_{\%}$ = 4 %. After elimination of fibers with a diameter higher than 500 nm, nanofibers average diameter is $\bar{d}_{I\ to\ 500}$ = 300 nm ±40 nm and $\bar{d}_{II\ to\ 500}$ = 270 nm ±40 nm.

The average diameter of electrospun TPU fibres (Fig. 7) is $\bar{d}_{I}$ = 245 nm ±40 nm and $\bar{d}_{II}$ = 375 nm ±95 nm then U = 55 kV, C = 3 wt. %. Then fibers with diameter up to 500 nm was eliminated, average diameter of nanofibers was $\bar{d}_{II\ to\ 500}$ = 245 nm ±65 nm. Analyzing the distribution of electrospun TPU fibers diameter obtained using U = 55 kV voltage (Fig. 7 (C = 3 wt.%)) we can see, that 100 % fibres with diameter 0 nm – 500 nm using I type electrode and 70 % fibres with diameter 0 nm – 500 nm were measured using II type of electrode. In this case 81 % nanofibers formed in the range 201 nm – 300 nm when using I type electrode. In Fig. 5 present that thinner TPU fibers was formed when II type electrode was used, but in Fig. 7 – thinner TPU fibers was formed, when I type electrode was used.

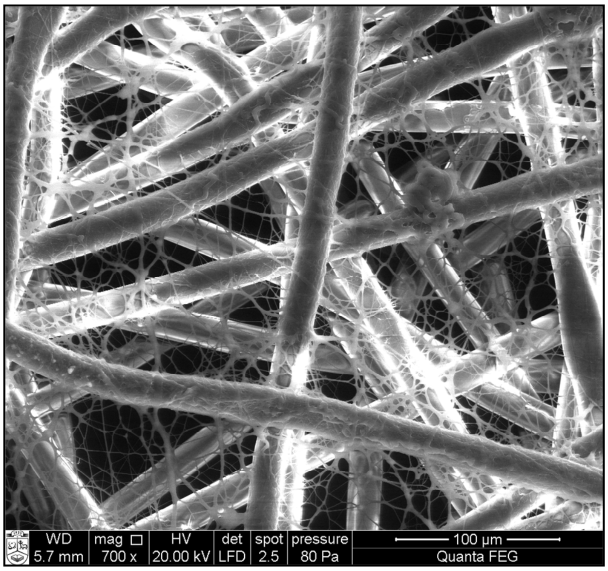
From all the presented results, we can state, that the type of electrode does not have significant influence on the diameter of electrospun TPU fibers. This showed the average diameter of electrospun TPU fibers after elimination of stick fibers.

SEM images present electrospun mat then C = 4 wt.% (Fig. 3, a, b) and C = 3 wt.% (Fig. 3, c, d), U = 65 kV. When concentration was 4 % thicker mat structure was obtained. In either case a porous mat is made from nanofibers and stick derivatives. It can be said that the concentration has influence on the TPU mat structure; the lower the concentration of solution, the rarer mat is formed.

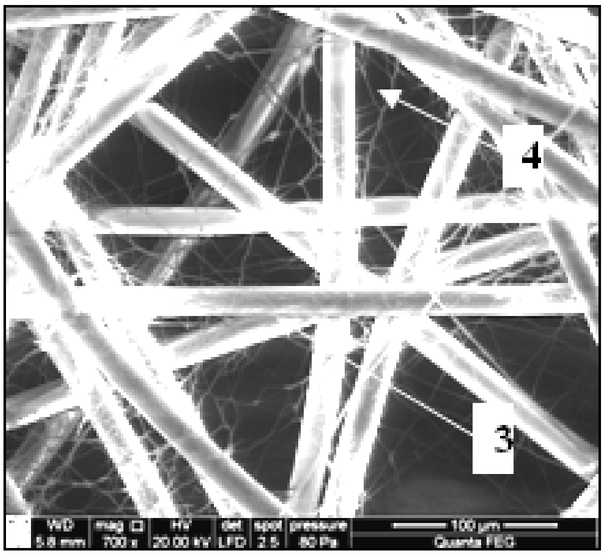
Comparing SEM images of electrospun mats using I type of electrode are presented in Fig. 6, a, (C = 4 wt.%) and Fig. 6, c, (C=3 wt.%). Thinner nanofibers were formed when C = 3 %. The average diameter of TPU fibers electrospun at C = 3 wt.% was $\bar{d}$ = 245 nm ±40 nm and at C = 4 wt.% was $\bar{d}$ = 350 nm ±65 nm. Then fibers with diameter higher than 500 nm was eliminated, average diameter of nanofibers at C = 4 wt.% was $\bar{d}_{to\ 500}$ = 300 nm ±80 nm.

Viscosity of polymers solution increases ns increasing concentration, so that is why thicker electrospun fibers are formed by electrospining process. These analyses and the results of other investigators justify, that solution concentration of solution has influence upon fibers diameter [17].

In Fig. 8 SEM images present electrospun thermoplastic polyurethane mats at C = 4 wt.%. The scale of images is 100 μm. From SEM images in Fig. 8 it can by noticed, that when applied voltage is 65 kV (Fig. 8, a) thinner porous mats were formed, than applying voltage 55 kV (Fig. 8, b). Increasing voltage increases the electric field between the electrodes, therefore more fibers were formed and thicker porous mat was formed.



a



b

Fig. 8. SEM images of electrospun TPU mats: a – U = 65 kV, II type electrode; b – U = 55 kV, II type electrode; 3 – fibers of support material, 4 – electrospun fibers

From presented SEM images it is possible to see, that at lower applied voltage less stick nanofiber are formed. The lower the applied voltage, the less the Taylor cones are formed and less nanofibers cover the support material.

CONCLUSIONS

- Dissolving TPU granules in mixed solvent of dimethylformamide and tetrahydrofuran (1 : 1, w/w) it is possible to form mat from micro/nanofibers by electrospinning process, but only with the electrode with the tines.
- After having calculated the average diameter of TPU fibers and the average diameter of TPU fibers when the stick fibers were eliminated the obtained results showed that the type of electrodes does not have significant influence on the average diameter of electrospun fibers. But the type of electrode has an influence on the electrospinning technological process. Using electrode with tines it is possible to form continuous flow of Taylor cones.
- Using TPU solution with concentration of 4 wt.% thicker mat, with thicker nanofibers was obtained than using TPU solution with concentration of 3 wt.%.
- Increasing of applied voltage, TPU mat with more stick fibers was formed.

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