Analysis of Structure of Electrospun Nonwoven Mats from Pure PCL Nano/Micro Fibres

Solveiga PUPKEVIČIŪTĖ, Erika ADOMAVIČIŪTĖ *, Sigitas STANYS

Department of Textile Technology, Kaunas University of Technology, Studentų St. 56, LT-51424 Kaunas, Lithuania

Electrospinning is a simple technique for the production of nano to micro scale fibers. Polycaprolactone (PCL) is biocompatible aliphatic polyester with many possible medical applications. PCL nanofibres, produced by electrospinning, could provide new characteristics that are of interest for medical applications. The aim of this study is to estimate the influence of solvents, solution concentrations, stirring duration of polymer solution and distance between the electrodes on structure of electrospun with "Nanospider™" equipment` PCL mats. To electrospun mats from PCL is possible, when PCL polymer is dissolved in chloroform or tetrahydrofuran solvents. It was investigated that structure of the electrospun nonwoven mats from PCL nano/microfibers depends on the concentration of polymer solution. Stirring duration of PCL solution only insignificant influences the structure of PCL electrospun mats. The distance between electrodes does not have influence on the diameter of electrospun PCL nano/ microfibers, but has influence on structure of electrospun mats.

Keywords: electrospinning, nano/microfibers, polycaprolactone PCL, "Nanospider™".

INTRODUCTION

Electrospinning has been known for over 60 years in the textile industry for manufacturing nonwoven fabrics. In recent years, there has been an increasing interest in exploiting this technology to produce nanoscale fibers. This is especially important in the fabrication of the nanofibrous scaffold for tissue engineering. This technique produces nonwoven mats with individual fiber diameters ranging from a few to hundreds nanometers. The fibers can be made to form a porous structure that is ideal for drug, gene as well as cell delivery [1, 2]. The spinning of fibers is achieved in a high voltage electric field. The high voltage causes the ejection of a polymer solution or melt, which forms a jet that moves from the spinneret towards the collecting area. Many factors, including physical variables, polymer and solvent nature, environmental conditions, collection of nanofibres method are known to affect the morphology and properties of electrospun fibers [3 – 9].

Typically, electrospinning is applicable to a wide range of polymers like those used in conventional spinning, i. e. polyolefines, polyamides, polyesters, aramide, acrylic as well as biopolymers like proteins, DNA, polypeptides, or others. The high specific surface area and small pore size of electrospun nanofibers make them interesting candidates for a wide variety of applications. Electrospun nonwoven mats have small pore size, high porosity and high surface area, therefore, it can be used in a wide variety of applications such as reinforcing fibers in composite materials, for scaffolds in tissue engineering, wound dressing, filters etc. [10, 11].

PCL is biocompatible aliphatic polyester with many possible applications in the medical field. It is one of the most commonly applied synthetic polymers for medical application because of its biocompatibility and slow biodegradability. The good solubility of PCL in solvents, its low melting point ($T = 59\,°C – 64\,°C$) and exceptional blend-compatibility with other polymers has stimulated extensive research into its potential application in the biomedical field. PCL is soluble in chloroform, tetrahydrofuran (TTH), dichloromethane (or methylene chloride (MC)), carbon tetrachloride, benzene, toluene, cyclohexanone and 2-nitropropane at room temperature [6, 12 – 16].

K. H. Lee et al. [11] investigated the effect of solvent on PCL electrospun nonwoven mats. PCL solution was dissolved in methylene chloride (MC), the fiber diameter of electrospun at 13 wt% of solution concentration was 5500 nm having a narrow diameter distribution. For solutions dissolved in the mixture of MC and dimethylformamide (DMF) the fiber diameter decreased by 200 nm. It was interpreted that DMF has not only a high dielectric constant, but also polyelectrolyte behavior, due to that thinner nanofibres were electrospun.

A. G. Kanani and et al. [6] investigated the effect of different solvents (glacial acetic acid, 90 % acetic acid, methylene chloride/dimethyl formamide (MC/DMF) (4/1), glacial formic acid and formic acid/acetone (4/1)) on electrospun PCL mats morphology, beads formation and fibres diameter. Nanofibres with almost uniform diameters were produced at 10 % and 15 % PCL concentrations when formic acid/acetone was used as a solvent.

Electrospun nonwoven mat from PCL nanofibres are excellent candidates for scaffolds in tissue engineering [17 – 20]. L. Ghasemi-Mobarakeh with co-authors [17] investigated a simple procedure such as alkaline hydrolysis of PCL nanofibrous scaffolds for improving its hydrophilicity and further attaching matrigel to them, to produce scaffolds suitable for nerve tissue engineering. Blending of matrigel with PCL solution did not appear to have any significant effect on hydrophilicity of scaffolds,

---
*Corresponding author. Tel.: +370-37-300223; fax: +370-37-353989.
E-mail address: *erika.adomaviciute@ktu.lt* (E. Adomavičiūtė)

cell proliferation, morphology and surface contact area [17]. L. Ghasemi-Mobarakeh et. al [18] investigated differentiation and proliferation of C17.2 cells on aligned and random PCL and PCL/gelatin nanofibrous scaffolds. The study results demonstrated that the properties of nanofibrous scaffolds were strongly influenced by the concentration of gelatin in the biocomposite. PCL/gelatin 70 : 30 nanofibers were selected for cell culture study as it provided better mechanical and biodegradation properties than PCL/gelatin 50 : 50 [18]. J. L. Lowery with co-authors [20] evaluated the effect of pore diameter on the proliferation of Human Dermal Fibroblast cells in PCL electrospun mats. Scaffold structure was found to have a significant impact on cell growth. In particular, pore size, or void size appears had greater impact on cell proliferation than did fiber size [20].

F. Chen et. al [19] reports on a novel surface modification technique of the PCL membrane by coating with electrospun nanofibers. The purpose of this study was to mimic the architecture of the natural extracellular matrix and create nanotopography for enhanced cellular attachment. A favorable cellular morphology and strong cell attachment was observed on the nanofibrous substrate after NaOH treatment. The surface modified PCL membrane offers promising applications in soft tissue engineering [19].

The studies have been done were PCL nanofibres were used as drug – carrier, for example, shikonin. A herbal medicine shikonin regarded as an effective compound associated with healing of wounds, scar, and burns, was successfully encapsulated in PCL/PTMC nanofibers using electrospinning [21].

In all above analyzed articles PCL nanofibres were fabricated using simple electrospinning equipment with syringe i. e., only small area of nonwoven mats was fabricated. The aim of this study is to form nonwoven material from PCL nanofibres by roller type "Nanospider TM" equipment and to investigate the influence of solvent type, solution concentration, solution stirring duration, distance between electrodes on structure of electrospun PCL mats.

MATERIALS AND METHODS

PCL (Aldrich Chemistry, $M_n \sim 10000$, $M_w \sim 14000$) polymer was attempted to dissolve in these organic solvents: chloroform, N,N-dimethylformamide (DMF), ethyl acetate, toluene, acetone, tetrahydrofuran (TTH).

Electrospinning solutions were prepared dissolving PCL polymer in solvents and stirred by magnetic stirring equipment Yellow Line MSH basic (Germany) without heating at room temperature. Surface tension of polymer solutions was determined by the tensiometer DCAT 21 (Germany). Viscosity of polymer solutions was determined by the funnel viscosimeter VZ-1 at room temperature. The principal of this method was to measure the time (s) in which 50 ml of the spinning solution flowed down through the hole with diameter 5.4 mm of funnel.

Nonwoven mats from PCL nano/microfibres were formed using „Nanospider^{TM}" (Elmarco, Czech Republic) electrospinning equipment (Fig. 1). Nonwoven mats from polymer solution were formed using electrode with tines. In electrospinning an electric field is applied between a grounded electrode (3) and electrode with tines (7). Due to the action of electrostatic forces the polymer solution on tines is distorted from a spherical drop to a Taylor cone. Once these forces overcome the surface tension of polymer solution a jet is drawn from the tip of the Taylor cone. As a result nonwoven material formed on support material – spunbond from polypropylene fibers (1). The main difference of "Nanospider ^{TM}" electrospinning equipment comparing with conventional (syringe) electrospinning equipment is the possibility to cover big amount of support material (1) by the layer of nano/microfibers. Contrary to conventional electrospinning equipments – here a jet of polymer solution travels from bottom electrode (6) to grounded electrode (3).
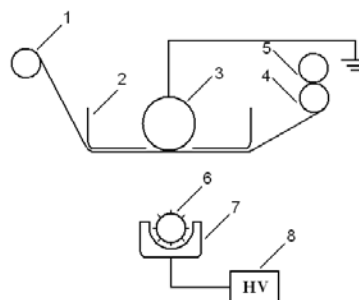

Fig. 1. "Nanospider^{TM}" electrospinning equipment: 1 – rollers of support material; 2 – frame of grounded electrode; 3 – 5 – rollers of support material with nonwoven mat; 6 – electrode with tines; 7 – tray with polymer solution; 8 – high voltage supply

During the experiments with PCL polymer solution applied voltage (U) was increased from 45 kV up to 65 kV, distance between electrodes (L) was 12 cm, 14 cm and 16 cm, the temperature of spinning solution was $T_{solution} = 18\,°C \pm 2\,°C$, the temperature of environment was $T = 20\,°C \pm 2\,°C$, air humidity was $\varphi = 42\,\% \pm 2\,\%$.

The structure of nonwoven mats was determined using scanning electron microscope SEM Quanta-200 (FEI, Netherlands). Digital image analysis using software Lucia Image 5.0 was used to evaluate diameter of nanofibres. The average of nano/microfibres diameter was calculated after measure all fibers in three SEM images with the scale of 5 μm and magnification of 20 000×.

RESULTS AND DISCUSSION

From literature review it is possible to notice, that PCL polymer may dissolve in many kinds of solvents [6, 12, 13, 22].

Table 1. Solubility of PCL polymer [22]

Solvent	PCL solubility
Tetrahydrofuran (TTH) C_4H_8O	soluble
N, N – Dimethylformamide (DMF) $HCON(CH_3)_2$	not soluble
Ethyl acetate $C_4H_8O_2$	not soluble
Toluene $C_3H_5CH_3$	partially soluble
Acetone C_3H_6O	not soluble
Chloroform $CHCl_3$	soluble

The solubility of used PCL polymer is presented in Table 1. PCL polymer is fully soluble at room temperature in solvents tetrahydrofuran (TTH) and chloroform.

To analyze the influence of solvents on structure of electrospun materials two types of polymer solutions were prepared: PCL solution of 20 % concentration in TTH and chloroform solvents was dissolved. In order to analyze the influence of DMF solvent on structure of PCL mat addition solution was prepared: 10 % concentration of PCL was dissolved in pure chloroform and 90/10 chloroform/DMF solvents (Table 2).

From data presented in Table 2 it is possible to note, that the type of solvent does not have influence on surface tension and viscosity of the prepared solutions.

Table 2. Average of surface tension ($\overline{\sigma}$) and viscosity ($\overline{\eta}$) of PCL solutions with different solvents [22]

Solution	$\overline{\sigma} \pm \Delta$, mN/m	$\overline{\eta} \pm \Delta$, s
20 % PCL in chloroform	32.69 ±0.11	10.26 ±1.31
20 % PCL in tetrahydrofuran	30.66 ±0.16	10.81 ±0.43
10 % PCL in chloroform	30.73 ±0.06	3.89 ±0.78
10 % PCL in chloroform/DMF (90/10)	30.87 ±0.22	4.10 ±0.80

a   b

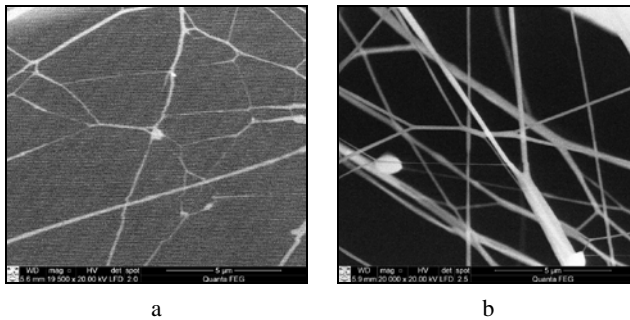**Fig. 2.** SEM images (scale 5µm) of electrospun PCL mats when solution concentration $C = 20$ %, applied voltage $U = 60$ kV, distance between electrodes $L = 12$ cm: a – PCL in TTH; b – PCL in chloroform. The duration of fibers collecting on support material $t = 60$ s

Nonwoven mats from PCL nano/microfibres of polymer solutions possible to form when PCL was dissolved in chloroform and TTH solvents (Fig. 2). In both cases electrospun mats with defects are visible: spots of polymer solutions on the surface of mat. Contrary to results presented by K. H. Lee et. al. [11] addition of DMF does not improve electrospinning process. It was impossible to electrospun a PCL mat, when DMF was added to solution. DMF block the formation of nanofibres on electrode with tines. It is believable that the reason to that is to high dielectric constant of DMF.

The average fibers diameter $\overline{d}$ electrospun from PCL in chloroform solution was $\overline{d}_{CH} = (206 \pm 25)$ nm, while those from PCL in TTH solution was $\overline{d}_{TTH} = (141 \pm 14)$ nm. Nonwoven mats with bigger amount of thin nanofibres were formed when as a solvent tetrahydrofuran was used (Fig. 3). 83 % of PCL nanofibers with diameter up to 200 nm were measured when solvent was tetrahydrofuran

and 65 % of PCL nanofibers – when solvent was chloroform. Microfibres with diameter over 500 nm were not formed from PCL in tetrahydrofuran solution (Fig. 3).
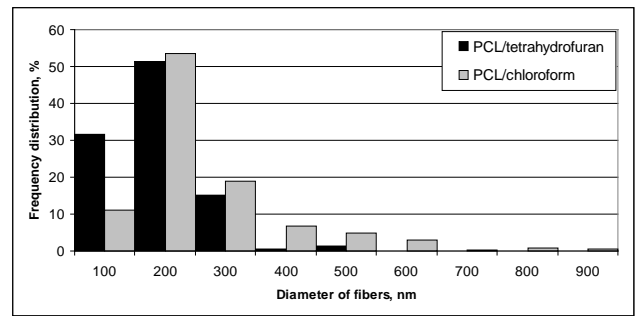

Fig. 3. The distribution of PCL fibers diameter electrospun from PCL (concentration $C = 20$ %) solution in chloroform (▪) and in TTH (■), applied voltage $U = 60$ kV, distance between electrodes $L = 12$ cm

From the data presented it is evident that nonwoven mat from pure PCL nano/microfibres is possible to form when PCL polymer is dissolved in chloroform or tetrahydrofuran solvents. Thinner PCL nanofibres can be formed from PCL polymer solution when was used more toxic solvent tetrahydrofuran.

The PCL polymer fully dissolved in chloroform after 1 h of solution stirring at room temperature by magnetic stirring equipment. In order to estimate the influence of PCL in chloroform solution preparation duration on structure of electrospun mats three types solutions with stirring duration for 1, 2 and 4 hours were prepared.

From the SEM images in Fig. 4 is possible to notice, that stirring duration of PCL solution does not have significant influence on structure of electrospun PCL mats. In all cases mats with many spots of polymer solution like those presented in Fig. 5 were electrospun.
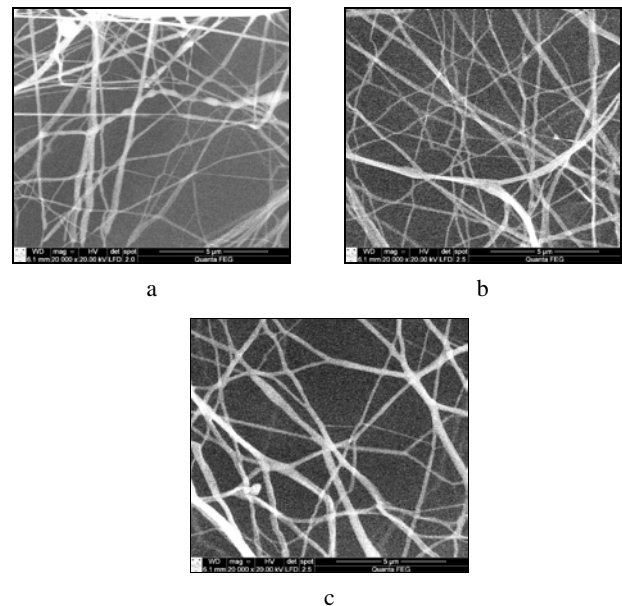

a   b

c

Fig. 4. SEM images (scale 5 µm) of electrospun PCL in chloroform mats (concentration $C = 10$ %) at applied voltage $U = 50$ kV, distance between electrodes $L = 12$ cm, solution stirring duration: a – 1 hour; b – 2 hour; c – 4 hour The duration of collecting fibers on support material $t = 60$ s
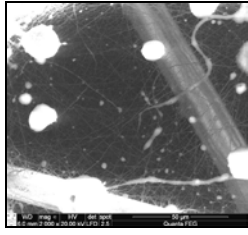
Fig. 5. SEM images (scale 50 µm) of electrospun PCL in chloroform mats (concentration $C = 10$ %) at applied voltage $U = 50$ kV, distance between electrodes $L = 12$ cm, solution stirring duration of 2 hours. The duration of collecting fibers on support material $t = 60$ s
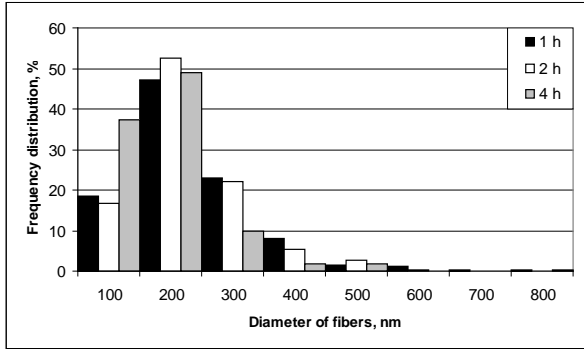

Fig. 6. The distribution of PCL fibers diameter electrospun from PCL in chloroform, concentration $C = 10$ %, at applied voltage $U = 50$ kV, distance between electrodes $L = 12$ cm, stirring duration 1 (■), 2 (□) and 4 (▨) hours

The average of PCL fibers electrospun with different stirring duration of polymer solution is $\overline{d}_{1\,h} = (183 \pm 19)$ nm, $\overline{d}_{2\,h} = (176 \pm 17)$ nm, $\overline{d}_{4\,h} = (134 \pm 15)$ nm. From the histogram (Fig. 6) we can see that bigger amount of nanofibres with diameter to 200 nm were formed from polymer solution after 4 hours of stirring duration (87 %). When PCL nanofibres were formed from polymer solution with stirring duration for 1 hour and 2 hours, the amount of nanofibres with diameter (0 – 200) nm are respectively 66 % and 70 %. From these results we can maintain that stirring duration of PCL in chloroform solution insignificant influences electrospun nanofibres diameter. The diameter of nanofibres has tendency to decrease with increase stirring duration of PCL solution.

To evaluate the influence of PCL solution concentration, nonwoven mats were formed from four types of polymer solution – PCL in chloroform with concentrations – $C = 10$ %, 15 %, 20 % and 25 %. Surface tension and viscosity of polymer solution with different concentration are presented in Table 3. From data presented in Table 3 we can see that surface tension has tendency to increase with increasing concentration of polymer solution. When concentration of PCL in chloroform increases from $C = 10$ % to $C = 25$ %, surface tension increases only about 10 %.

The viscosity of investigated solutions significantly increase with increasing concentration of polymer solution. When concentration of PCL in chloroform increases from $C = 10$ % to $C = 25$ %, the viscosity of solution increases more than 80 %.

Table 3. Average of surface tension ($\overline{\sigma}$) and viscosity ($\overline{\eta}$) of PCL solutions with different concentrations

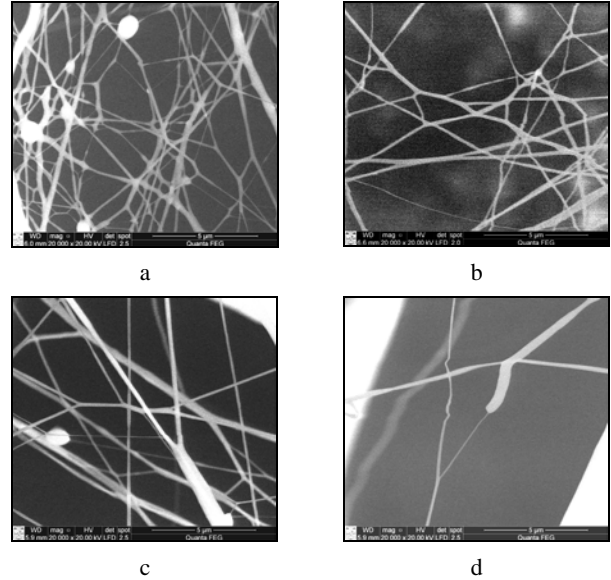| Solution	$\overline{\sigma} \pm \Delta$, mN/m	$\overline{\eta} \pm \Delta$, s
10 % PCL in chloroform	30.73 ±0.06	3.89 ±0.78
15 % PCL in chloroform	32.29 ±0.08	7.06 ±0.15
20 % PCL in chloroform	32.69 ±0.11	10.26 ±1.31
25 % PCL in chloroform	34.17 ±0.23	29.02 ±2.46

Fig. 7. SEM images (scale 5 µm) of electrospun PCL in chloroform mats at applied voltage $U = 60$ kV, distance between electrodes $L = 12$ cm, concentration of PCL solutions C, %: a – 10; b – 15; c – 20; d – 25. The duration of collecting fibers on support material $t = 60$ s

From SEM images presented in Fig. 7 it is seen that with increase of PCL solution concentration in chloroform amount of collected PCL nanofibres on support material decreases. The average of PCL fibers diameter electrospun from different concentration of PCL solution in chloroform is $\overline{d}_{10\,\%} = (147 \pm 18)$ nm, $\overline{d}_{15\,\%} = (184 \pm 22)$ nm, $\overline{d}_{20\,\%} = (206 \pm 25)$ nm, $\overline{d}_{25\,\%} = (258 \pm 27)$ nm, i. e. with increase of concentration of PCL solution, the diameter of electrospun fibers increase also. The data presented in histogram (Fig. 8) shows that 80 % of nanofibres with diameter to 200 nm were formed from $C = 10$ % polymer solution. The amount of nanofibres with diameter up to 200 nm from polymer solution with different concentration $C = 15$ %, 20 % and 25 % are respectively 67 %, 65 % and 45 %. From these result we can conclude that thinner nanofibres were formed from polymer solution with concentration $C = 10$ %. Such results can be explained that increasing concentration of PCL in chloroform solution, results in increase of solution viscosity, therefore the diameter of electrospun PCL nanofibres increases too and rare electrospun mat is formed. The same results were obtained as PCL was dissolved in MC/DMF (4/1), glacial acetic acid, 90 % acetic acid, dichloromethane (DCM) and methanol [6, 7].
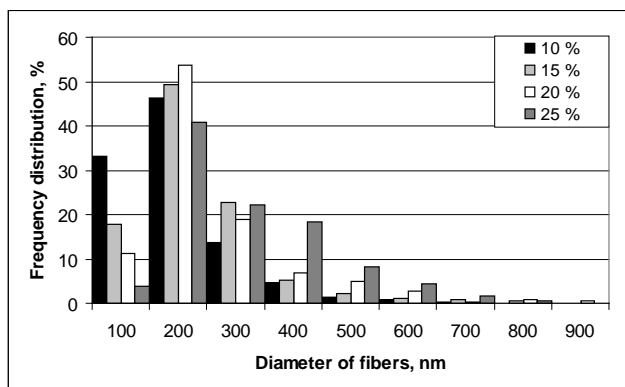
Fig. 8. The distribution of PCL fibers diameter of elektrospun from PCL in chloroform at applied voltage $U = 60$ kV, distance between electrodes $L = 12$ cm, concentrations C of PCL solutions: ■ – 10 %, ■ – 15 %, □ – 20 %, ■ –25 %

When from polymer solution on electrode with tines are formed a jet, it moves towards the collecting area, meanwhile solvent evaporate and a jet (nanofibres) solidify. To evaluate the influence of distance between electrodes on structure of electrospun PCL nonwoven mats investigation was performed when distance between the electrodes was 12 cm, 14 cm and 16 cm.

In Fig. 9 SEM images of electrospun PCL mats are presented, when the distance between the electrodes are different. As it can be seen from the SEM images amount of nanofibres has tendency to decrease with increasing distance between the electrodes. It can be explained that decreasing distance between the electrodes electric field strength increases, and amount of formed nano/microfibres increases.
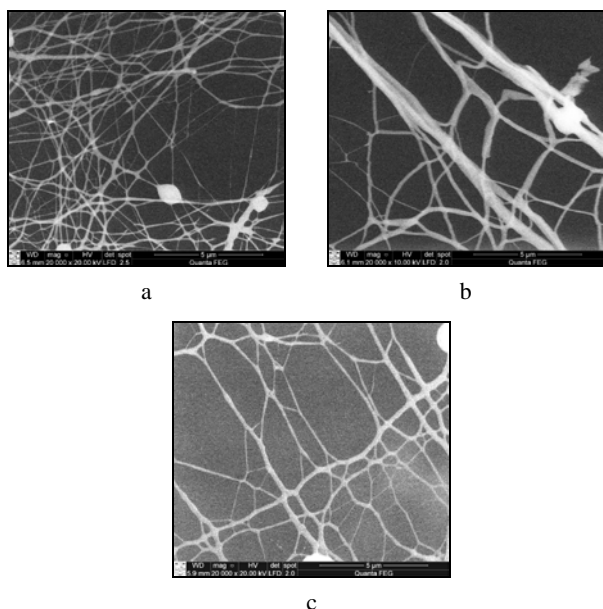

Fig. 9. SEM images (scale 5 µm) of electrospun PCL in chloroform mats (concentration $C = 10$ %) at applied voltage $U = 60$ kV, distance between electrodes L: a – 12 cm; b – 14 cm; c – 16 cm. The duration of collecting fibers on support material $t = 60$ s
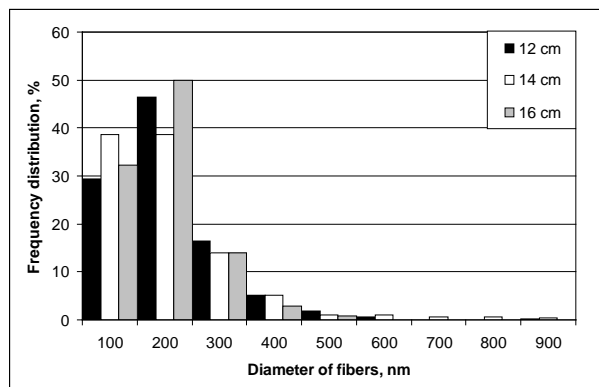

Fig. 10. The distribution of PCL fibers diameter electrospun from PCL in chloroform solution concentration $C = 10$ %, applied voltage $U = 60$ kV, distance between electrodes L: ■ – 12 cm; □ – 14 cm, ■ – 16 cm

The average of PCL fibers electrospun with different distance between electrodes was $\bar{d}_{12\,cm} = (158 \pm 18)$ nm, $\bar{d}_{14\,cm} = (158 \pm 23)$ nm, $\bar{d}_{16\,cm} = (142 \pm 14)$ nm. From average of fibers diameter and histogram presented in Fig. 10 it is evident that the distance between the electrodes has only insignificant influence on nanofiber diameter. The 76 % of nanofibres with diameter to 200 nm were formed when distance between electrodes $L = 12$ cm. 77 % and 83 % of nanofibres with diameter up to 200 nm were formed when distance between electrodes was respectively $L = 14$ cm and 16 cm. The distance between electrodes has marginally influence only on amount of electrospun nano/microfibres on support material.

CONCLUSIONS

1. To electrospun mat from pure PCL nano/microfibres it is possible, when PCL polymer is dissolved in pure in chloroform or tetrahydrofuran. Nonwoven mat from more thinner nanofibres is formed from PCL dissolved in tetrahydrofuran.
2. Stirring duration of PCL solution has no significant influence on structure of PCL electrospun mats. It was noticed, that stirring duration influences PCL nanofibers diameter. The diameter of PCL nanofibres has tendency to decrease with increasing the stirring duration.
3. The structure of electrospun nonwoven mats from pure PCL nano/microfibers depends on the concentration of solution. Rarer nonwoven mat with thicker nano/microfibers was electrospun from more viscous (higher concentration) PCL solution in chloroform.
4. The distance between electrodes only insignificantly influences variation of the diameter of electrospun PCL nano/microfibers, but has influence on structure of electrospun mats. At lower distance between the electrodes (at higher strength of electrical field) density of electrospun PCL mats has tendency to increase.

REFERENCES

1. **Chong, E. J., Phan, T. T., Lim, I. J., Zhang, Y. Z., Bay, B. H., Ramakrishna, S., Lim, C. T.** Evaluation of Electrospun PCL/gelatin Nanofibrous Scaffold for Wound Healing and Layered Dermal Reconstitution *Acta Biomaterialia* 3 2007: pp. 321 – 330.

2. **Bhardwaj, N., Kundu, S. C.** Electrospinning: A Fascinating Fiber Fabrication Technique *Biotechnology Advances* 28 2010: pp. 325 – 347.
http://dx.doi.org/10.1016/j.biotechadv.2010.01.004

3. **Gaumer, J., Prasas, A., Lee, D., Lannutti, J.** Structure-function Relationships and Source-to-Ground Distance in Electrospun Polycaprolactone *Acta Biomaterialia* 9 2009: pp. 1552 – 1561.

4. **Marras, S. I., Kladi, K. P., Tsivintzelis, I., Zuburtikudis, I., Panayiotou, C.** Biodegradable Polymer Nanocomposites: The Role of Nanoclays on the Thermomechanical Characteristics and the Electrospun Fibrous Structure *Acta Biomaterialia* 4 2008: pp. 756 – 765.

5. **Adomavičiūtė, E., Milašius, R., Levinskas, R.** The Influence of Main Technological Parameters on the Diameter of Poly(vinyl alcohol) (PVA) Nanofibre and Morphology of Manufactured Mat *Materials Science (Medžiagotyra)* 13 (2) 2007: pp. 152 – 155.

6. **Kanani, A. G., Bahrami, S. H.** Effect of Changing Solvents on Poly (ε-caprolactone) Nanofibrous Webs Morphology *Journal of Nanomaterials* 2011 doi:10.1155/2011/724153.
http://dx.doi.org/10.1155/2011/724153

7. **Beachley, V., Wen, X.** Effect of Electrospinning Parameters on the Nanofiber Diameter and Length *Materials Science and Engineering C* 29 2009: pp. 663 – 668.
http://dx.doi.org/10.1016/j.msec.2008.10.037

8. **Adomavičiūtė, E., Stanys, S.** Formation of Electrospun PVA Mats on Different Types of Support Materials Using Various Kinds of Grounded Electrodes *Fibres & Textiles in Eastern Europe* 19 (4) 2011: pp. 34 – 40.

9. **Adomavičiūtė, E., Stanys, S., Banuškevičiūtė, A., Milašius, R.** Influence of the Shape of the Bottom Rotating Electrode on the Structure of Electrospun Mats *Fibres & Textiles in Eastern Europe* 18 (6) 2010: pp. 49 – 53.

10. **Frenot, A., Chronakis, I. S.** Polymer Nanofibers Assembled by Electrospinning *Current Opinion in Colloid and Interface Science* 8 2003: pp. 64 – 75.
http://dx.doi.org/10.1016/S1359-0294(03)00004-9

11. **Lee, K. H., Kim, H. Y., Khil, M. S., Ra, Y. M., Lee, D. R.** Characterization of Nano-Structured Poly(1-caprolactone) Nonwoven Mats via Electrospinning *Polymer* 44 2003: pp. 1287 – 1294.

12. **Van der Schueren, L., De Schoenmaker, B., Kalaoglu, Ö. I., De Clerck, K.** An Alternative Solvent System for the Steady State Electrospinning of Polycaprolactone *European Polymer Journal* 47 2011: pp. 1256 – 1263.

13. **Woodruff, M. A., Hutmacher, D. W.** The Return of a Forgotten Polymer—Polycaprolactone in the 21st Century *Progress in Polymer Science* 35 2010: pp. 1217 – 1256.
http://dx.doi.org/10.1016/j.progpolymsci.2010.04.002

14. **Mavis, B., Demirtas, T. T.** Synthesis, Characterization and Osteoblastic Activity of Polycaprolactone Nanofibers Coated with Biomimetic Calcium Phosphate *Acta Biomateriale* 5 2009: pp. 3098 – 3111.

15. **Reneker, D. H., Kataphinan, W., Theron, A.** Nanofiber Garlands of Polycaprolactone by Electrospinning *Polymer* 43 2002: pp. 6785 – 6794.

16. **Kenawy, E. R., Abdel-Hay, F. I., El-Newehy, M. H.** Processing of Polymer Nanofibers Through Electrospinning as Drug Delivery Systems *Materials Chemistry and Physics* 113 2009: pp. 269 – 302.

17. **Ghasemi-Mobarakeh, L., Prabhakaran, M.P., Morshed, M., Nasr-Esfahani, M. H., Ramakrishna, S.** Bio-functionalized PCL Nanofibrous Scaffolds for Nerve Tissue Engineering *Materials Science and Engineering C* 30 2010: pp. 1129 – 1136.
http://dx.doi.org/10.1016/j.msec.2010.06.004

18. **Ghasemi-Mobarakeh, L., Prabhakaran, M. P., Morshed, M., Nasr-Esfahani, M. H., Ramakrishna, S.** Electrospun Poly(3-caprolactone)/Gelatin Nanofibrous Scaffolds for Nerve Tissue Engineering *Biomaterials* 29 2008: pp. 4532 – 4539.

19. **Chen, F., Lee, C. N., Teoh, S. H.** Nanofibrous Modification on Ultra-thin Poly(e-caprolactone) Membrane via Electrospinning *Materials Science and Engineering C* 27 2007: pp. 325 – 332.
http://dx.doi.org/10.1016/j.msec.2006.05.004

20. **Lowery, J. L., Datta, N., Rutledge, G. C.** Effect of Fiber Diameter, Pore Size and Seeding Method on Growth of Human Dermal Fibroblasts in Electrospun Poly(ε-caprolactone) Fibrous Mats *Biomaterials* 31 2010: pp. 491 – 504.
http://dx.doi.org/10.1016/j.biomaterials.2009.09.072

21. **Han, J., Chen, T. C., Branford-White, C. J., Zhu, L. M.** Electrospun Shikonin-loaded PCL/PTMC Composite Fiber Mats with Potential Biomedical Applications *International Journal of Pharmaceutics* 382 2009: pp. 215 – 221.

22. **Pupkevičiūtė, S., Adomavičiūtė, E., Milašiūtė, L., Stanys, S.** The Formation of Polycaprolactone Nanofibers by Electrospinning *Technologies and Design of Garments. Book of Conference Materials* 2011: pp. 244 – 247 (in Lithuanian).