

DESIGN OF A NOVEL NOZZLE PROTOTYPE FOR INCREASED PRODUCTIVITY AND IMPROVED COATING QUALITY DURING ELECTROSPINNING

ELEKTROEĞİRME PROSESİNDE ÜRETİM ARTIŞI VE KAPLAMA KALİTESİNİN İYİLEŞTİRİLMESİNE YÖNELİK YENİ NOZÜL DİZAYNI ÇALIŞMASI

Nuray UÇAR¹, Mehmet UÇAR², Nuray KIZILDAĞ^{1*}

¹*Istanbul Technical University, Department of Textile Engineering, Istanbul, Turkey*

²*Kocaeli University, Department of Machine Design and Manufacturing, Izmit, Turkey*

Received: 22.02.2013

Accepted: 15.04.2013

ABSTRACT

In the last ten years, the market and studies related with nanofibers are considerably increasing in the areas such as filtration, energy harvesting, medical textile. Electrospinning is one of the most widely used techniques for nanofiber production. Mainly, two different types of electrodes in the electrospinning process are used: one is the conventional narrow nozzle and the other is the nozzle-less system. Conventional narrow nozzle is not preferred at industrial applications due to several problems such as low productivity, non-homogeneous coating and clogging. It is mostly preferred at laboratory applications, because of low price, wide production range and easy use. However, main disadvantages of nozzle-less system are high price (cost) and narrow production flexibility (range) compared to conventional narrow nozzle system. In this study, new novel nozzle prototype has been designed and studied to eliminate the disadvantages of conventional narrow nozzle system. From trials, it has been seen that production increased about 3 times compared to conventional narrow nozzle system, while homogenous coating could be obtained without clogging problem. It has also very low cost compared to nozzle-less system.

Key Words: Electrospinning, Nanofiber, Nozzle.

ÖZET

Geçtiğimiz son 10 yıl içerisinde, nanolif ile ilgili çalışmalar ve pazar payları (filtre, enerji, tıbbi tekstil vb alanları da kapsayacak şekilde) hızlı bir şekilde artmaktadır. Elektroegirme sistemi, yaygın olarak kullanılan nanolif üretim tekniklerinden biridir. Temelde, elektroegirme sisteminde iki tip elektrot kullanılmaktadır, şöyle ki; dar uçlu (iğne tipli) nozul sistemi ve nozulsüz sistem. Konvansiyonel dar uçlu nozul sistemi endüstriyel ölçekli üretimlerde, bazı dezavantajlarından ötürü (düşük üretim, homojen olmayan kaplama ve uçların sıklıkla tıkanması gibi) pek tercih edilmemektedir. Diğer taraftan, dar uçlu nozul sistemlerin, düşük maliyeti, oldukça esnek ve çok çeşitli üretim tiplerini üretebiliyor olması ve kullanım kolaylığı, laboratuvar ölçekli uygulamalarda tercih edilmesine sebebiyet vermektedir. Nozulsüz sistemin en temel dezavantajı ise oldukça yüksek bir fiyata sahip olması ve üretim esnekliğinin (çeşitliliğinin) dar uçlu nozul sistemindeki kadar geniş olmamasıdır. Bu çalışmada, konvansiyonel dar uçlu nozul sisteminin dezavantajlarını yok edecek şekilde yeni bir prototip nozul sistemi dizayn edilmiştir. Gerçekleştirilen deneysel çalışmalar sonucunda, konvansiyonel dar uçlu nozul sistemine kıyasla yaklaşık 3 kat üretimin arttığı, son derece homojen yüzey kaplamanın, nozul tıkanması ile karşılaşmadan gerçekleştiği ve nozulsüz sisteme kıyasla oldukça düşük bir maliyete sahip olabileceği görülmüştür.

Anahtar Kelimeler: Elektroegirme, Nanolif, Nozul.

Corresponding Author: Nuray Kızıldağ, kizildagn@itu.edu.tr, Tel: +90 212 293 13 00, Fax: +90 212 251 88 29

1. INTRODUCTION

Electrospinning is a fiber spinning technique which is based on the ultrafine fiber drawing from polymer solution jets by applying electrical

forces (1). On conventional electrospinning with nozzle, polymer solution or melt that has to be spun is forced through a syringe pump to form a pendant drop of the polymer at the tip of the nozzle. High voltage potential

is applied to the nozzle, thereby inducing free charges into the polymer solution. These charged ions move in response to the applied electric field towards the electrode of opposite polarity and thus transfer tensile forces

to the polymer liquid. The pendant polymer drop takes a cone like form at the tip of the capillary with the effect of the electric field. And, when the applied potential overcomes the surface tension of the liquid, a jet of liquid is ejected from the cone tip which then undergoes an instability and elongation process (2,3). As the jet travels through the atmosphere, the solvent evaporates, and the ultrafine, dry fibers accumulates on the collector as a nanoweb (4,5). Electrospinning is attracting great interest, because not only can it produce polymer fibers with small diameters in the submicron or nanometer level, but also has the advantages of being simple and convenient (6,7). Electrospinning as an effective and promising technique for the production of nanofibers, provides a mat of extremely fine fibers with small pore size, high surface area and high porosity which is advantageous in a wide variety of applications such as high performance filters, biomedical applications, separation membranes, reinforcement in composite materials, templates for the preparation of functional nanotubes, protective clothing, sensors and many others (8-12). Despite this variety in potential applications, nanofibers have been commercially applied in only a few fields such as filters, artificial vessels, wound dressings, etc. For the expansion of the application fields of nanowebs, a production technology which will scale up the nanoweb production to industrial level is necessary (13,14). Today, most nanofiber producers as well as research institutes have constructed their own electrospinning equipment. NanoStatics (US), Kato Tech Co. Ltd.

(Japan), Fulence Co. Ltd. (Japan), E-spin Nanotech Pvt. Ltd. (India), Inovenso Ltd. (Turkey) are manufacturers of electrospinning equipments which are generally used for laboratory applications. Nanospider™ Technology, which has been developed by the Technical University of Liberec and Elmarco Company, was applied to the industrial production of nanofibers in 2006.

The major handicap for industrial level production is the production rate (9,15), which is typically 0.3 g/nozzle/hour for a conventional single nozzle electrospinning system (10,16). The efforts to scale up the electrospinning technology to an industrial production level have been mainly focused on the multiplication of the jets using multi-nozzle constructions (17-31). The principle of multi-nozzle electrospinning is based on an idea to feed multiple nozzles from a single source of the polymer solution (13). The needle configuration, number of needles and needle gauge are the important factors to be taken into consideration when designing multi-nozzle electrospinning constructions. Needles can be arranged in different configurations such as linear, elliptical, circular, triangular, square or hexagonal (10). In Figure 1a, the multi-nozzle electrospinning head developed by NanoStatics Company is shown. In Figure 1b, the schematic of a multi-nozzle electrospinning head developed by Toptec Company and in Figure 1c the multi-nozzle electrospinning head used in Nanospinner 24 developed by Inovenso Ltd. (Turkey) is illustrated.

In the multi-nozzle electrospinning, the jet distribution depends on the design

of nozzle arrangement. Although multi-nozzle electrospinning provides an increase in production if properly designed, the mismatch between natural jet distribution and the mechanical structure leads to instabilities in the process (13,17). During electrospinning from multi-nozzles, many problems such as nonhomogeneous web structure, uneven fiber deposition, different behaviors of different jets, inactive nozzles and dripping are encountered all of which are due to interference of the adjacent electric fields. In some studies an auxiliary electrode is suggested which makes the system more complex (10,17,19-31). Furthermore, electrospinning from multiple nozzles may be inconvenient due to the blocking (clogging) tendency of the nozzles (33). With an attempt to increase fiber production rate and fabricate fibers over extended surface areas, nozzle-less or free surface electrospinning has been developed (34,35). In nozzle-less electrospinning, a rotating drum is dipped into a bath of liquid polymer as schematically presented in Figure 2a. The thin layer of polymer on the rotating drum surface is exposed to a high voltage electric field. When the voltage exceeds a critical value, a number of electrospinning jets whose number and location is set up naturally in their optimal positions are generated (36) as presented in Figure 2b. The natural distribution of the jets enables the formation of higher number of jets from a small area (16) and thus higher packing density and web uniformity. Several types of rotating electrodes have been developed for nozzle-less electrospinning some of which are illustrated in Figure 2c.

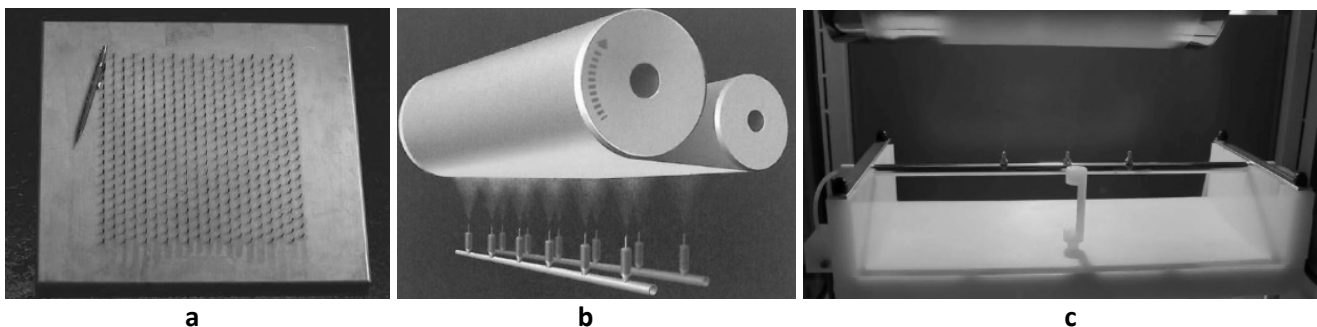


Figure 1. a. Photograph of a multi-nozzle spinning head by NanoStatics; b. Schematic of a multi-nozzle spinning head by Toptec (13); c. Photograph of a multi-nozzle electrospinning head used in Nanospinner 24 developed by Inovenso Ltd. (Turkey) (32).

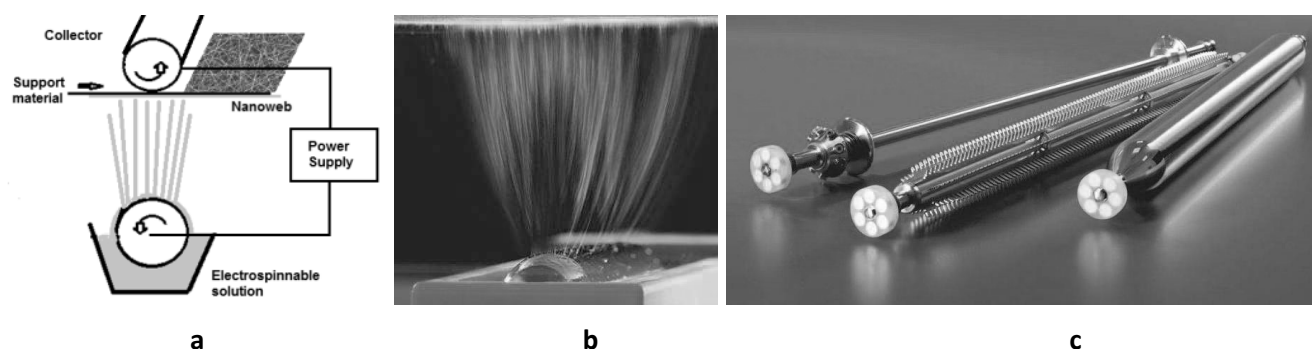


Figure 2. a. Schematic of free liquid surface electrospinning (36,37); b. Photograph showing free liquid surface electrospinning from a rotating electrode (13); c. various types of electrodes developed for nozzleless electrospinning (13).

Unlike the conventional electrospinning setup which uses a single nozzle with applied electrical voltages of 15-30 kV, the voltages used for nozzle-less spinning can exceed 50 kV (13). Despite its high price, it is preferred in industrial applications due to its high production rate, homogeneous web formation and clogging-free process. On the other hand the fiber diameter distribution can be large when spinning occurs from the free polymer surface (33).

In this study, an alternative novel nozzle prototype which combines the advantages of single nozzle and nozzle-less electrospinning systems has been designed and developed. The new nozzle prototype which is very simple and economical to use is developed for increased productivity and homogeneous coating.

2. EXPERIMENTAL

Electrospinning solutions were prepared by dissolving PAN in N,N-dimethylformamide (DMF) using a

magnetic stirrer. Polymer solution concentration was 10% (w/w) in DMF. Electrospinning of nanofibers was performed on a horizontal electrospinning setup schematic design of which is illustrated in Figure 3.

It consisted of a feeding unit, a high voltage power supply capable of 0–30 kV, and a grounded rotating collector. Upon applying a high voltage, fluid jets ejected from the tip of the nozzle and accelerated towards the collector, which was placed at 15 cm from the nozzle. The solvent evaporated and nanofibers were collected on the collector. Nanofiber production was conducted using two different nozzle types, i.e., one is two conventional narrow nozzles (multiple narrow nozzles) and the other is the new nozzle developed for increased productivity and homogeneous coating. The photographs of the new nozzle developed are presented in Figure 4.

As can be seen from the figure, when the new nozzle is used, the polymer

solution is drawn by high voltage electric field, not just only from the groove (channel) which the polymer solution is fed but also from a whole surface with 1.5 cm length which polymer solution is available.

The appearance of the nanofibers has been examined by optical microscope (Olympus BX51 with 1000x magnification).

In order to investigate the blocking (clogging) problem of nozzles, another polymer solution which often causes clogging problems on conventional narrow nozzles has been used, i.e.; 10 % Mah Elastomer (Polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene-*graft*-maleic anhydride) in a solvent mixture of 70% Cyclohexane, 20% DMF, 10% tetrahydrofuran (THF). Mah Elastomer, purchased from Sigma Aldrich, is a triblock copolymer and is mainly used as a component of hot melt adhesives, sealants and modifier for polymers, thermosets and general rubber compounding.

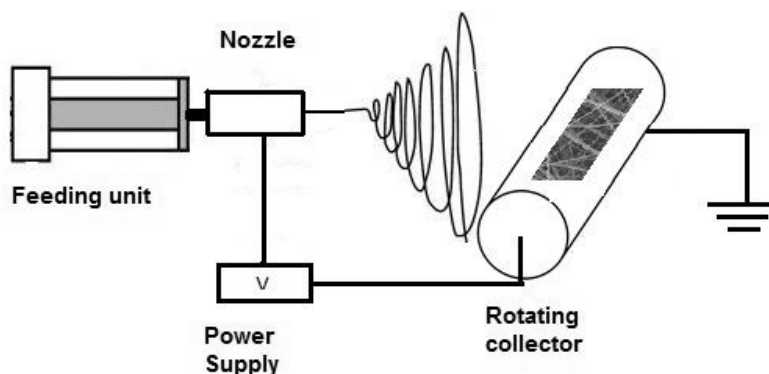


Figure 3. Schematic of electrospinning setup used to produce nanofibers

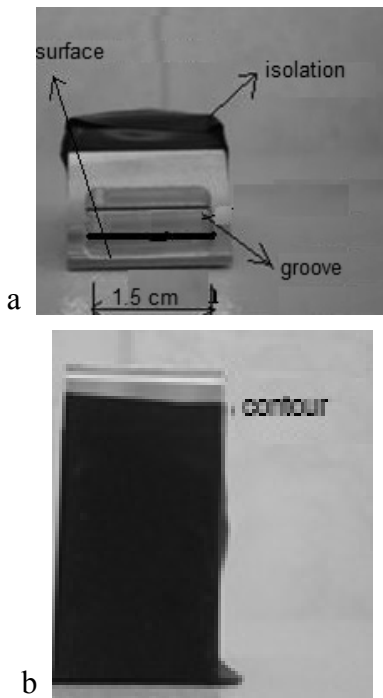


Figure 4. Photographs of the new nozzle developed a. front view; b. bottom view

Results and Discussion

Photographs showing electrospinning PAN nanofiber using two conventional narrow nozzles and the new nozzle are presented in Figure 5a and 5b respectively.

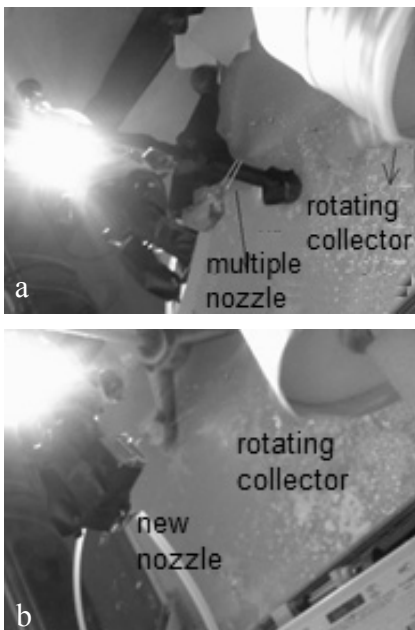


Figure 5. Electrospinning with a. two conventional narrow nozzles; b. one new nozzle

Figure 6 shows the photographs of the nanofiber coatings obtained after 10 minutes of electrospinning. As can be seen from the figures, while a non-

homogeneous surface coating was obtained from conventional two narrow nozzle system, very homogenous coating was obtained from the new nozzle system which provided the formation of multiple jets on the nozzle surface, the number and location of which were set up naturally in their optimal positions.

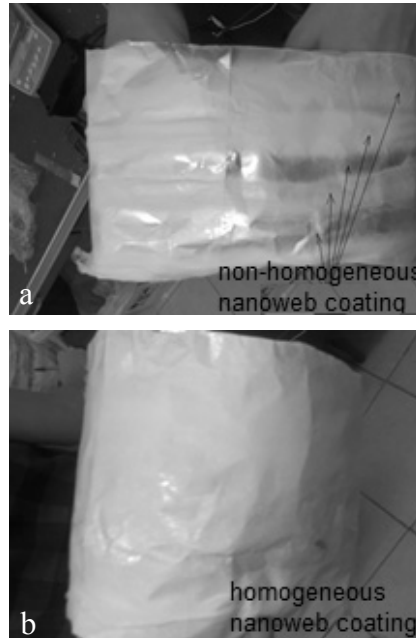


Figure 6. Nanoweb formation with a. conventional two narrow nozzles; b. one new nozzle

The image taken by optical microscope and a photograph of the nanoweb obtained is presented in Figure 7 and 8, respectively. As seen from the Figure 7, nanofiber web from PAN could be successfully produced. The diameter of the fibers produced with the new nozzle was in the range of nanometers (the scale bar on the photograph is 20 micrometer).

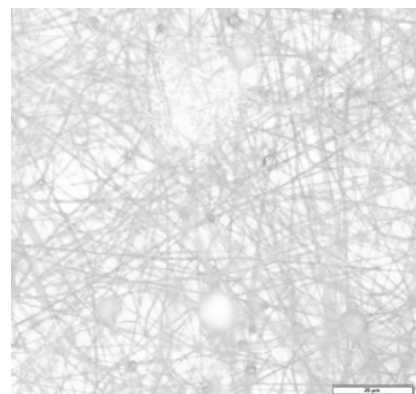


Figure 7. Optical microscope image (with 1000 times magnification) of the nanoweb produced with the new nozzle



Figure 8. Nanoweb obtained using the new nozzle

Nanofiber formation could be achieved with the high voltage of 25kV and a feeding rate of 7 ml/h when working with the new nozzle while 20 kV high voltage and 4 ml/h feeding rate was used to produce nanofibers when working with the conventional nozzles. The new nozzle with its wide groove and wide surface making more polymer solution available for drawing yields to formation of many jets leading an increase of production rate. Higher applied voltage and higher feeding rate also supports to an increase of production rate. When the production rates were compared after 10 minutes of electrospinning, the new nozzle showed an increase of about 3 times when compared to the conventional nozzle. The information about production is given in Table 1.

In order to investigate the blocking (clogging) problem of the new nozzle, another polymer solution which causes often clogging problem on conventional narrow nozzle has been used, i.e.; 10 % MAH Elastomer. Thus another advantage was obtained with use of the new nozzle i.e.; during 10 minute production, there was no clogging with the new nozzle system, whereas many cloggings were observed with the conventional nozzle each of which stopped the electrospinning process (Table 1).

Table 1. Comparison of the conventional nozzle and the new nozzle regarding the production and clogging

Nozzle type	Nanofiber amount with PAN after 10 minutes (g)	Cloggings with MAH Elastomer
Conventional nozzle	0.05	many times
New nozzle	0.15	no

3. CONCLUSIONS

A new nozzle prototype was designed for use in electrospinning. The main advantage of the nozzle was the increase in the production rate. Besides the increase in the feeding rate and also a little increase in the applied voltage, the main reason for this was that the new nozzle with its wide groove and wide surface enabled the formation of many jets which were set up naturally. Additionally, the new nozzle resulted in the formation of a

homogeneous web structure. No clogging was observed in the evaluation time when electrospinning with the new nozzle, while the process was interrupted many times due to the clogging of the nozzles when electrospinning with two conventional narrow nozzles.

The new nozzle is suggested for use in electrospinning with increased productivity, continuous process, homogeneous coating, larger coating width compared to two conventional

narrow nozzles, together with very reasonable cost compared to nozzle-less system. In the future; further studies will be conducted for the new nozzle, such as morphological analysis of the products obtained from different types of polymer solutions, analysis of the effect of different geometrical structure and dimension and number of the new nozzle on the electrospun nanoweb and the electrospinning process.

REFERENCES

1. Itoh, H., Chan, K.H.K., Kotaki, M., 2011, "Structure and morphology of nylon 6 fibers produced by nozzle-less electrospinning", *Annual Technical Conference - ANTEC, Conference Proceedings*, 2, 1121-1124.
2. Ramakrishna, S., Fujihara, K., Teo, W. E., 2005, "An Introduction to Electrospinning and Nanofibers", *World Scientific Publishing Company, Incorporated, River Edge, NJ, USA*. Retrieved from <http://0-site.ebrary.com.divit.library.itu.edu.tr>.
3. Zheng, M.H., Zhang, Y.Z., Kotakic, M., 2003, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites", *Composites Science and Technology*, 63, 2223-2253.
4. Thandavamoorthy S., Bhat, G.S., Tock, R.W., 2005, "Electrospinning of Nanofibers", *Journal of Applied Polymer Science*, 96, 557-569.
5. Chen C., Chuanbao, C., Xilan, M., 2006, "Preparation of non-woven mats from all-aqueous silk fibroin solution with electrospinning method", *Polymer*, 47, 6322-6327.
6. Lee, S., Obendorf, S. K., 2006, "Developing protective textile materials as barriers to liquid penetration using melt-electrospinning", *Journal of Applied Polymer Science*, 102, 4, 3430-3437.
7. Kong, C.S., 2009, "Multi-jet ejection and fluctuation in electrospinning of polyvinyl alcohol with various nozzle diameters", *Polymer Engineering and Science*, 49, 11, 2286-2287.
8. Bagherzadeh, R., Latifi, M., Najar, S.S., 2012, "Transport properties of multi-layer fabric based on electrospun nanofiber mats as a breathable barrier textile material", *Textile Research Journal*, 82, 1, 70-76.
9. Yang, L.E., 2005, "Study on Multiple Nozzles Electrospinning", *PQDT*.
10. Nayak, R., Padhye, R., Kyrtatzis, I.L., 2011, "Recent advances in nanofibre fabrication techniques", *Textile Research Journal*, 82, 2, 129-147.
11. Ucar, N., Ayaz, O., Oksuz, M., 2011, "Production of Elastomeric Polymer fiber Web by Electrospinning Process, *Tekstil ve Konfeksiyon*, 21(1), 10-15.
12. Ucar, N., Ayaz, O., Bahar, E., 2012, "Thermal and mechanical properties of composite nanofiber webs and films containing cellulose nanowhiskers", *Textile Research Journal*, first published on June 26, 2012 as doi:10.1177/0040517512450761
13. Stanislav, P., "Industrial Production Technology for Nanofibers", http://cdn.intechopen.com/pdfs/23289/InTech-Industrial_production_technology_f_or_nanofibers.pdf (10.02.2013)
14. Varesano, A., Rombaldoni, F., Mazzuchetti, G., 2010, "Multi-jet nozzle electrospinning on textile substrates: observations on process and nanofibre mat deposition", *Polymer International*, 59, 12, 1606-1615.
15. Enlong, Y., Jingjing, S., Yuan, X., 2010, "Influence of electric field interference on double nozzles electrospinning", *Journal of Applied Polymer Science*, 116, 6, 3688-3692.
16. Pirjo Heikkiläe, "Nanostructured Fiber Composites, and Materials for Air filtration", Doctoral Thesis, Tampere University of Technology.
17. Bowman, J., Taylor, M., Sharma, V., 2003, "Multispinneret methodologies for high throughput electrospun nanofiber", *Materials Research Society, Warrendale, PA*, 15-20.
18. Ding, B., Kimura, E., Sato, T., 2004, "Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning", *Polymer*, 45, 1895-1902.
19. Theron, S., Yarin, A., Zussman, E., 2005, "Multiple jets in electrospinning: Experiment and modeling", *Polymer*, 46, 2889-2899.
20. Teo, W., Gopal, R., Ramaseshan, R., 2007, "A dynamic liquid support system for continuous electrospun yarn fabrication", *Polymer*, 48, 3400-3405.
21. Regele, J., Papac, M., Rickard, M., 2002, "Effects of capillary spacing on EHD spraying from an array of cone jets", *Journal of Aerosol Science*, 33, 1471-1479.
22. Lee, J.R., Jee, S.Y., Kim, H.J., 2006, KR Patent WO2006123879.
23. Kim, G.H., Cho, Y.S., Kim, W.D., 2006, "Stability analysis for multi-jets electrospinning process modified with a cylindrical electrode", *European Polymer Journal*, 42, 2031-2038.
24. Tomaszewski, W., Szadkowski, M., 2005, "Investigation of electrospinning with the use of a multi-jet electrospinning head", *Fibres Textiles Eastern Europe*, 13, 22.
25. Bocanegra, R., Galan, D., Marquez, M., 2005, "Multiple electrosprays emitted from an array of holes", *Journal of Aerosol Science*, 36, 1387-1399.
26. Yamashita, Y., Ko, F., Miyake, H., 2008, "Establishment of nanofiber preparation technique by electrospinning", *Sen'i Gakkaishi*, 64, 24-28.
27. Varesano, A., Carletto, R.A., Mazzuchetti, G., 2009, "Experimental investigations on the multi-jet electrospinning process", *Journal of Materials Processing Technology*, 209, 5178-5185.
28. Varesano, A., Rombaldoni, F., Mazzuchetti, G., 2010, "Multi-jet nozzle electrospinning on textile substrates: Observations on process and nanofibre mat deposition", *Polymer International*, 59, 1606-1615.
29. Yang, Y., Jia, Z., Li, Q., 2006, "Multiple jets in electrospinning", *8th International Conference on Properties and Applications of Dielectric Materials*, 940-940.
30. Kim, H., Park, J., 2007, A bottom-up electrospinning device, EP Patent 1,740,743, 2007
31. Yang, Y., Jia, Z., Li, Q., 2010, "A shield ring enhanced equilateral hexagon distributed multi-needle electrospinning spinneret", *IEEE Trans Dielectrics Electrical Insulation*, 17, 1592-1601.
32. <http://www.inovenso.com/portfolio-view/nanospinner24/> (20.02.2013)
33. Dosunmu, O.O., Chase, G.G., Kataphinan, W., 2006, "Electrospinning of polymer nanofibres from multiple jets on a porous tubular surface", *Nanotechnology*, 17(4), 1123-1127.
34. Jirsak, O., Sanetnik, F., Lukas, D., 2009, "Method of nanofibres production from a polymer solution using electrostatic spinning and a device for carrying out the method" US Patent 7,585,437, 2009
35. Jirsak, O., Sanetnik, F., Lukas, D., 2005, WO2005-024101. Patent (Czech Republic).
36. Patrick, S., Maly, M., "Production Nozzle-Less Electrospinning Nanofiber Technology", <http://www.elmarco.com/upload/soubory/dokumenty/66-1-1-mrs-fall-boston-09.pdf>, (20.02.2013)
37. http://www.czechtechnologydays.org/sites/default/files/28_Mr.%20Nomoto_Elmarco.pdf, The 5 th Czech-Japan Technology Days, 25 May 2010 Tokyo (20.02.2013).