TECHNICKÁ UNIVERZITA V LIBERCI
Fakulta textilní

Význam beztryskového elektrostatického zvlákňování pro rozvoj průmyslové výroby a aplikací nanovlákenných materiálů

Habilitační práce

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Obsah

1. Úvod

Objev a následná úspěšná komercializace beztryskového elektrostatického zvlákňování znamenaly v poslední dekádě dramatický nárůst zájmu o nanovlákenné materiály s unikátními vlastnostmi, které se takřka „přes noc" staly ekonomicky dostupnými pro průmyslovou výrobu. Nanovlákna se změnila z vědecké kuriozity na reálný základ mnoha produktů. Uchazeč měl to štěstí, že se mohl aktivně účastnit tohoto vzrušujícího procesu transformace výsledků akademického výzkumu do nového průmyslového odvětví, které vychází z oboru technických – netkaných textilií, ale zasahuje mnoho dalších oblastí, od filtrací plynů a kapalin po biomedicínské aplikace.

Samotný proces vývoje technologie ze stádia funkčního vzorku do stádia sériové výroby produkčních linek přináší kromě ekonomických a technických problémů i překvapivé množství vědeckých témat. Příkladem může být potřeba maximalizace výkonu produkční linky při minimálním celkovém objemu stroje. Triviální přístup založený na zvětšování koncentrace elektrod přináší spíše opačný efekt, a tak hlubší porozumění technologickému procesu vede k využití nástrojů teorie elektromagnetického pole, mechaniky tekutin, termodynamiky a dalších oborů. Podobně stabilita kvality výroby nanovlákenných materiálů závisí na pochopení a zvládnutí dynamických jevů, jako je rychlá změna koncentrace polymerního roztoku, proces odpařování rozpouštědel a jejich odstraňování ze zvlákňovacího prostoru, (ne)rovnoměrnost proudění vzduchu, vliv teploty a vlhkosti, atd.

Ještě větší množství vědeckých problémů přináší výzkum a vývoj aplikací nanovláken. Tak například tradiční oblast, kde se nanovlákna uplatňují už desítky let – filtrace a separace, je stále předmětem intenzivního výzkumu jak vlastních mechanizmů filtrace a separace, tak porozumění struktuře materiálu nanovláken, jejich povrchu a metodám ovlivnění hydrofobních nebo hydrofilních vlastností, atd. Mnoho aplikací je stále ve stadiu základního výzkumu, například aplikace nanovláken z anorganických materiálů (elektrody baterií, solárních a palivových článků), nanovláken z biopolymerů pro medicínu (tkáňové inženýrství, systémy uvolňování léčiv), nebo speciálních nanovláken pro senzory a kompozitní materiály.

Předkládaná habilitační práce ilustruje příspěvek uchazeče ve výzkumu průmyslové technologie pro výrobu nanovláken a s tím souvisejícími aplikacemi za posledních přibližně deset let. Práce je souborem vybraných publikací z oblasti technologie a aplikací nanovlákenných materiálů. Při tomto způsobu prezentace se nelze vyhnout opakování některých informací v úvodních částech článků. Uchazeč věří, že tento fakt nebude čitatele nadměrně obtěžovat a neubere na srozumitelnosti práce.

2. Beztryskové elektrostatické zvlákňování jako průmyslová technologie (výkon, stabilita, kvalita produkce)

První část habilitační práce tvoří dvě publikace, které se zabývají využitím beztryskového elektrostatického zvlákňování (elektrospiningu) jako průmyslové výrobní technologie.

V první publikaci je uvedena diskuse přístupů k fyzikálnímu popisu procesu beztryskového elektrospiningu. Zatímco proces dloužení vláken v elektrostatickém poli byl relativně úspěšně popsán a je stejný bez ohledu na způsob iniciace (z trysek nebo z volné hladiny kapalného polymeru), zásadním přínosem bylo pochopení tvorby Taylorových kuželů na volné hladině (popsané D. Lukášem a spol.).
Z citovaného modelu vyplývá velká výhoda beztryskové technologie: „samonastavení“ optimální prostorové periody zdrojů vláken. Z fyzikální podstaty jevu navíc vyplývá i rovnoměrnost procesu podél zvlákňovací elektrody.

Publikace 1 přináší původní výsledky především v experimentální části, kde jsou uvedeny parametry průmyslové technologie realizované stroji Nanospider™. Jako produktové parametry vyráběného materiálu byly zvoleny filtrační vlastnosti kompozitního média složeného z komerčního filtračního papíru s nanesenou nanovlákennou vrstvou z Polyamidu 6. Z publikovaných grafů vyplývá, že beztryskový proces dosahuje velmi vyrovnané kvality jak v prostoru (příčný profil role), tak v čase. V práci jsou dále uvedeny výkony průmyslových linek v několika konfiguracích pro výrobu médií pro filtraci vzduchu.

Publikace 2 tvoří první kapitolu monografie zaměřené na nanosystémy pro uvolňování (distribuci) funkčních částic, především v biomedicíně. Průmyslová dostupnost a produktivita technologie je i v tomto případě velmi významným faktorem, který ovlivňuje rozhodování investorů o zavedení nových technologií na trh. Publikace je zaměřena především na kritické porovnání beztryskového elektrospiningu, „klasického“ multi-tryskového elektrospiningu a alternativních technologií, které konkurují především výkonem.

2.1. Publikace 1:

Petrik, S. – Maly, M.: **Production Nozzle-Less Electrospinning Nanofiber Technology.** In: Mater. Res. Soc. Symp. Proc. Vol. 1240, 2010, Materials Research Society, 1240-WW03-07, 2010 (doi:10.1557/PROC-1240-WW03-07).

Oponovaný článek ve sborníku symposia Materials Research Society (MRS Fall Meeting, Boston, MA, November 30-December 4, 2009), vydaný Cambridge University Press, 2010.

Uchazeč přednesl vyžádanou přednášku na toto téma a předsedal sekci WW2: Methods of Processing of Polymer Nanofibers I.

Přínos uchazeče:

Analýza a porovnání teoretických modelů elektrostatického zvlákňování (tvorba nanovláken, beztryskový přístup) v kontextu technologie v průmyslovém měřítku. Kritické porovnání alternativních způsobů výroby nanovláken. Metodické vedení průmyslových experimentů, sběr a vyhodnocení experimentálních výsledků, vyhodnocení parametrů technologie Nanospider (rovnoměrnost výroby a produktových vlastností filtračních materiálů s nanovlákennou vrstvou).

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Production Nozzle-Less Electrospinning Nanofiber Technology

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ABSTRACT

The theoretical background and technical capabilities of the free liquid surface (nozzle-less) electrospinnig process is described. The process is the basis of both laboratory and industrial production machines known as Nanospider^{TM} and developed by Elmarco s.r.o. Technical capabilities of the machines (productivity, nanofiber layer metrics, and quality) are described in detail.

Comparison with competing/complementary technologies is given, e.g. nozzle electrospinning, nano-meltblown, and islets-in-the sea. Application fields for nanofiber materials produced by various methods are discussed. Consistency of the technology performance and production capabilities are demonstrated using an example of polyamide nanofiber air filter media.

INTRODUCTION

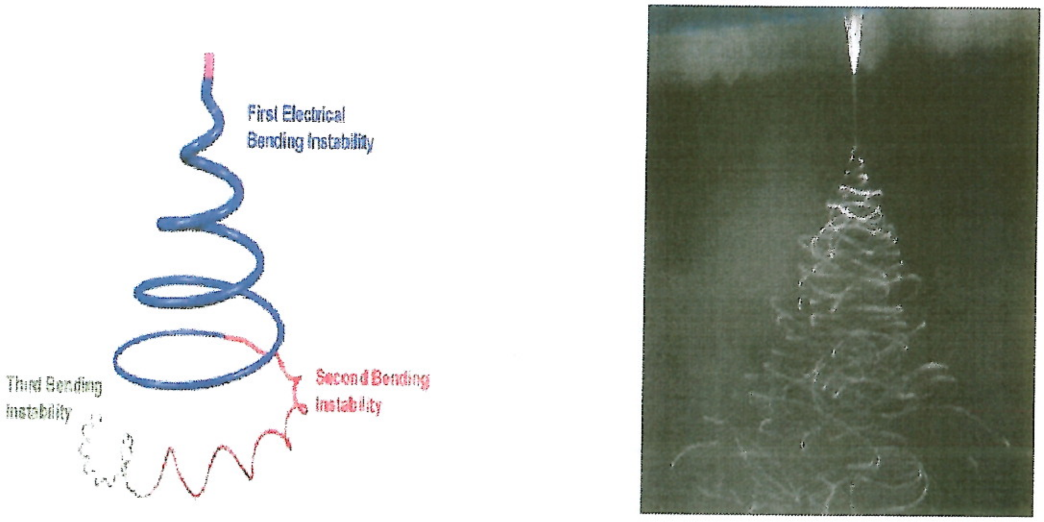
Electrospinning methods for creating nanofibers from polymer solutions have been known for decades [1, 2]. The nozzle-less (free liquid surface) technology opened new economically viable possibilities to produce nanofiber layers in a mass industrial scale, and was developed in the past decade [3]. Hundreds of laboratories are currently active in the research of electrospinning process, nanofiber materials, and their applications. Nanofiber nonwoven-structured layers are ideal for creating novel composite materials by combining them with usual nonwovens. The most developed application of this kind of materials is air filtration [4]. liquid filters and separators are being developed intensively with very encouraging results. Also well known are several bio-medical applications utilizing nanofiber materials, often from biocompatible/degradable polymers like PLA, gelatine, collagen, chitosan. These developing applications include wound care, skin-, vessel-, bone- scaffolds, drug delivery systems and many others. [3, 5]. Inorganic/ceramic nanofibers attract growing interest as materials for energy generation and storage (solar and fuel cells, batteries), and catalytic materials [6-10].

To fully explore the extraordinary number of application opportunities of nanofibers, the availability of reliable industrial-level production technology is essential. This paper intends to demonstrate that the technology has matured to this stage.

THEORETICAL BACKGROUND

The electrospinning process is an interesting and well-characterized physical phenomenon and has been an attractive subject for theoretical investigations of several groups [9, 11-17, 1, 2]. Most work concentrates on the essentials of the process – the nanofiber formation from a liquid polymer jet in a (longitudinal) electric field. It has been theoretically described and experimentally proven that the dominant mechanism is whipping elongation occurring due to bending instability [13, 16, 17]. Secondary splitting of the liquid polymer streams can occur also [1], but the final thinning process is elongation.

In Figure 1, the schematic of bending mechanism derived from physical model (a) is compared with a stroboscopic snapshot (b) [18].



a **b**

Figure 1. The path of an electrospinning jet (a – schematic, b – stroboscopic photograph).
(Courtesy of Darrell Reneker, University of Akron)

A comprehensive analysis (electrohydrodynamic model) of the fiber formation mechanisms published by Hohman et al. [16, 17] describes the regions of individual kinds of instability observed during the process. It has predicted and experimentally proven that there is a domain of the process variables where bending instability dominates, as illustrated in Figure 2.

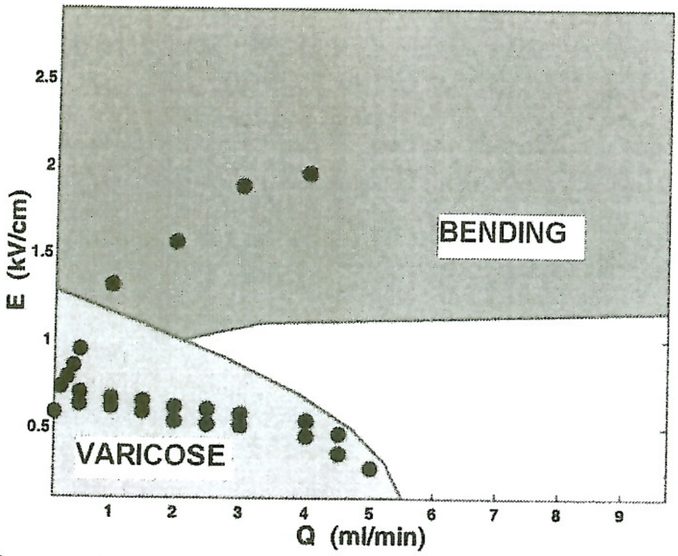


Figure 2. Operating diagram for a PEO jet. The upper shaded region shows the onset of the whipping instability, the lower one shows the onset of the varicose instability [17].

The efforts to scale up the electrospinning technology to an industrial production level used to be based on multiplication of the jets using multi-nozzle constructions [1]. However, the number of jets needed to reach economically acceptable productivity is very high, typically thousands. This brings into play many challenging task, generally related to reliability, quality consistency, and machine maintenance (especially cleaning). The nozzle-less electrospinning solves most of these problems due to its mechanical simplicity, however, the process itself is more complex because of its spontaneous multi-jet nature. The Lukas' et al. [19] study focused on the process of multi-jet generation from a free liquid surface in an electric field. They showed that the process can be analyzed using Euler's equations for liquid surface waves

$$\nabla\left(\rho\frac{\partial\Phi}{\partial t}+p\right)=0 \qquad (1)$$

where Φ is the scalar velocity potential, p is the hydrostatic pressure, and ρ is the liquid density. They derived the dispersion law for the waves in the form

$$\omega^2=(\rho g+\gamma k^2-\varepsilon E_0^2 k)\frac{k}{\rho} \qquad (2)$$

where E_0 is electric field strength, γ – surface tension.

The relationship between angular frequency ω and wave number k is in Figure 3, electric field is the parameter. When a critical electric field intensity is reached (E_c, curve 1), ω^2 is turned to be negative, ω is then a purely imaginary value, and hence, the amplitude of the liquid surface wave

$$\xi = Ae^{qt}\exp(ikx) \qquad (3)$$

exponentially grows, which leads to an instability.

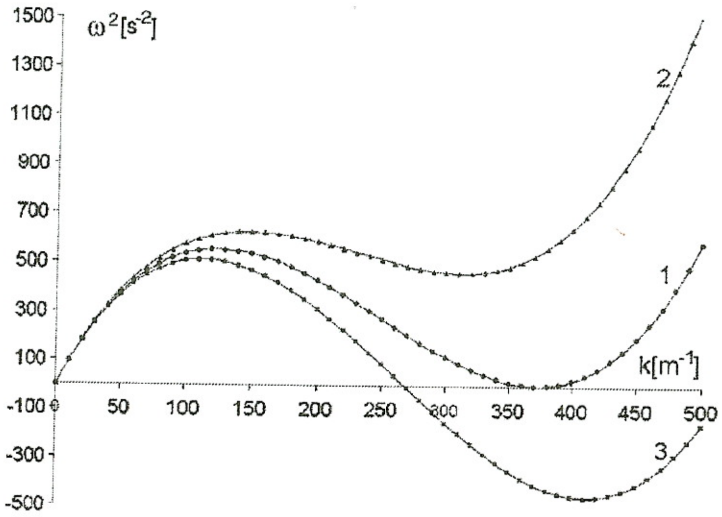


Figure 3. Relationship between the square of the angular frequency and the wave number for distilled water, electric field is the parameter 1: $E=E_c$=2.461 945 094x10^6 V/m, 2: E=2.4x10^6 V/m, and 3: E=2.5x10^6 V/m [19]

Critical field strength can then be expressed

$$E_c = \sqrt[4]{4\gamma\rho g/\varepsilon^2} \qquad (4)$$

From this equation, they derived the expression for the critical spatial period („wavelength") – the average distance between individual jets emerging from the liquid surface (Figure 4).

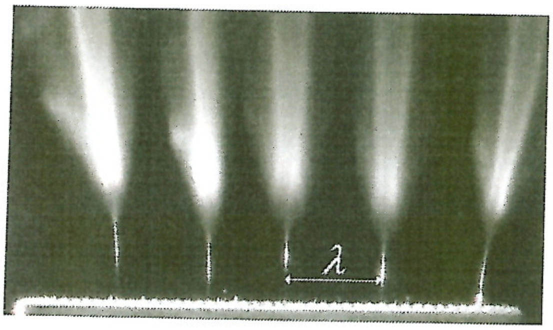
$$\lambda_c = 2\pi/k_c = 2\pi a \qquad (5)$$

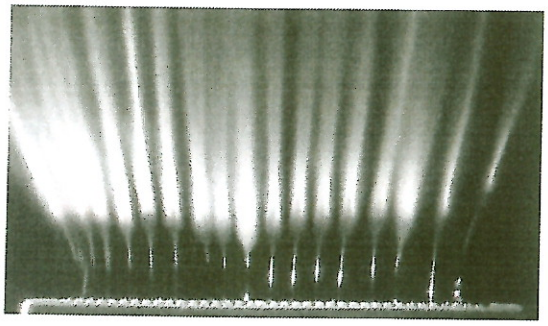
and

$$\lambda = 12\pi\gamma/[2\varepsilon E_0^2 + \sqrt{(2\varepsilon E_0^2)^2 - 12\gamma\rho g}] \qquad (6)$$

a is the capillary length

$$a = \sqrt{\gamma/\rho g} \qquad (7)$$





a b

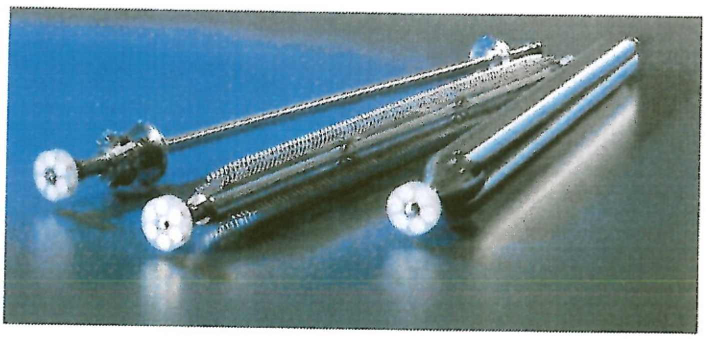
Figure 4. Free liquid surface electrospinning of Polyvinyalcohol at 32 kV (a) and 43 kV (b)
(Courtesy of David Lukas, Technical University of Liberec)

TECHNICAL REALIZATION AND DISCUSSION

Description of the nozzle-less technology

The simplest realization of the nozzle-less electrospinning head is in Figure 5. A rotating drum is dipped into a bath of liquid polymer. The thin layer of polymer is carried on the drum surface and exposed to a high voltage electric field. If the voltage exceeds the critical value (4), a number of electrospinning jets are generated. The jets are distributed over the electrode surface with periodicity given by equation (6). This is one of the main advantages of nozzle-less electrospinning: the number and location of the jets is set up naturally in their optimal positions. In the case of multi-needle spinning heads, the jet distribution is made artificially. The mismatch between "natural" jet distribution and the real mechanical structure leads to instabilities in the process, and to the production of nanofiber layers which are not homogenous.

Several types of rotating electrodes for free liquid surface electrospinning for industrial machines have been developed (Figure 5b). However, the drum type is still one of the most productive.



a b

Figure 5. Free liquid surface electrospinning from a rotating electrode (a) and various types of spinning electrodes (b)

Table 1. Comparison of Nozzle vs. Nozzle-Less Electrospinning

Production variable	**Nozzle**	**Nozzle-Less**
Mechanism	Needle forces polymer downwards. Drips and issues deposited in web.	Polymer is held in bath, even distribution is maintained on electrode via rotation.
Hydrostatic pressure	Production variable – required to be kept level across all needles in process.	None.
Voltage	5 – 20 kV	30 – 120 kV
Taylor cone separation	Defined mechanically by needle distances.	Nature self-optimizes distance between Taylor cones (Eq. (6)).
Polymer concentration	Often 10% of solution.	Often 20% or more of solution.
Fiber diameters	80, 100, 150, 200, 250 and higher. Standard deviation likely to vary over fiber length.	80, 100, 150, 200, 250 and higher. Standard deviation of +/- 30%.

Table 2. Nanofiber Production Methods

	Extrusion		**Electrospinning**	
Sub-type	Fine hole	Islets-in-the-sea	Nozzle	Nozzle-Less
Description	Fine fiber meltblown process, melted polymer is forced through small holes	Polymer blends are extruded through thicker holes, then separated afterwards, often hydro-entangled	Solvent polymers are forced through a needle and formed through an electrostatic field	Electrostatic field is used to form fibers but is formed without needles using higher voltage on roller-electrodes
Voltage	n/a	n/a	5 – 20 kV	30 – 120 kV
Fiber size (nm)	800 – 2,500 s = +/- 200%	800 – 2,500 s = +/- 200%	?? – 500 s = Varies	80 – 500 s = +/- 30%
Hydrostatic pressure	Yes	Yes	Yes	No
Production ready?	Yes	Yes	No	Yes

Research and development centers are very active in their efforts to further improve productivity of the manufacturing process. Novel methods for the production of sub-micron fibers are being developed. The most advanced methods ("Fine Hole" meltblown and "Islets-in-the-sea") are compared with the two current electrospinning approaches in Table 2. The individual methods can be considered to be complementary rather than competing. This is especially true with respect to the fiber diameter distribution and fiber layer uniformity. Individual methods will likely find different areas of application. More productive Nano-meltblown and Islets-in-the-sea technologies compromise fiber diameter and homogeneity and will likely be used in production cost sensitive applications like hygiene nonwovens, while high quality electrospun technologies will be used in products where their high added value and need for low amounts of the material can be easily implemented (air and liquid filtration, biomedicine).

The nozzle-less principle using rotating electrodes has been developed into a commercially available industrial scale. A photograph of a modular Nanospider ™ machine is in Figure 6.

Figure 6. Nozzle-less production electrospinning line (Nanospider™)

Performance of the technology

In addition to productivity (or throughput) of the production line, individual industrial applications require certain production consistency. We will illustrate the nozzle-less electrospinning technology performance with the example of air filtration media composed of a regular cellulose substrate and a thin nanofiber layer made from Polyamide 6. The product can be characterized by a number of parameters, like fiber diameter distribution (mean value and its standard deviation), basis weight of the nanofiber layer, etc. For the particular application, functional product parameters are more important. Typical values are the initial gravimetric filtration efficiency (IGE), differential filtration efficiency, and pressure drop, measured according to the norms widely accepted within industry.

The correlation between nanofiber diameter and basis weight of the nanofiber layer with differential filtration efficiency is illustrated in Figure 7. To obtain various basis weights, substrate speed was varied from 0.2 m/min to 4 m/min for each series of samples. Polymer solution parameters (concentration, etc.) together with electric field intensity determine the range of nanofiber diameter. Nanofiber diameter distribution has been measured using a scanning electron microscope (SEM). Basis weight values were obtained either by using an analytical scale Mettler (higher values), or by extrapolation from its known dependence on substrate velocity (lower ones).

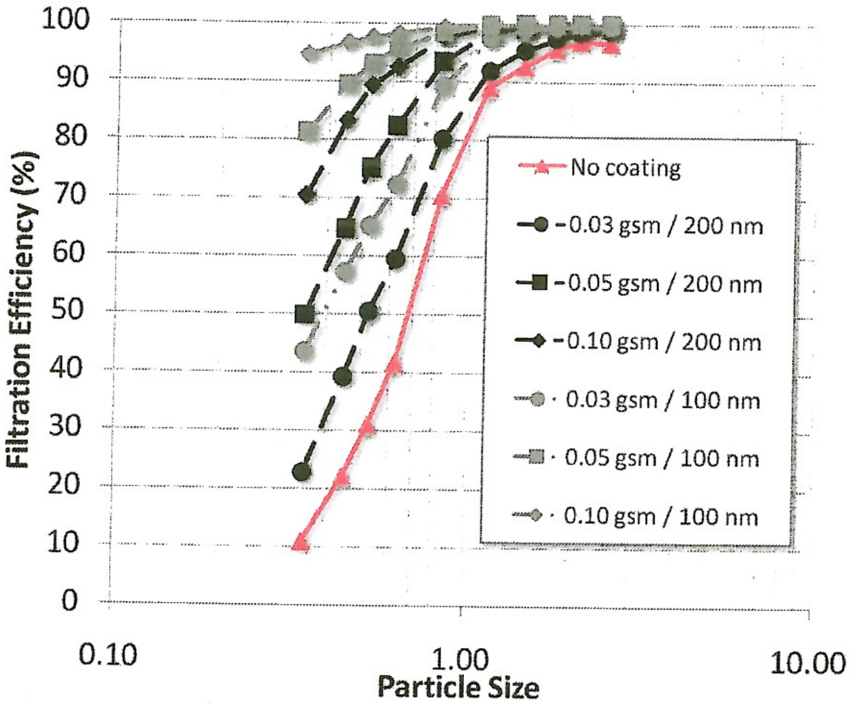


Figure 7. Filtration efficiency of nanofiber media samples

Table 3. Properties of nanofiber filtration media samples shown in Figure 7

Pressure drop for various coatings at 32 ft/min face velocity (equivalent to 490 ft/min based on pleated filter)						
Substrate	*Basis Weight*	*NF Diameter*	*Filtration Efficiency*		*Pressure Drop*	
	(g/m^2)	(nm)	at 0.35 micron particle size (%)	D vs. uncoated substrate	(mm of H_20)	D vs. uncoated substrate
Cellulose	No coating	n/a	11	n/a	15.24	n/a
Cellulose	0.03	200	23	108%	17.53	15%
Cellulose	0.05	200	50	357%	19.30	27%
Cellulose	0.10	200	70	545%	24.13	58%
Cellulose	0.03	100	44	298%	18.80	23%
Cellulose	0.05	100	81	644%	22.61	48%
Cellulose	0.10	100	95	766%	29.21	92%

Pressure drop and initial gravimetric filtration efficiency have been chosen as representative product parameters. They were measured using NaCl aerosol at the following settings: air flow speed: 5 m/min, sample area 100 cm^2, flow rate 50 l/min.

In Figure 8, results of long-term stability and reproducibility of the IGE are presented. It can be seen that the individual runs differ within the standard deviation of the process, and the mean value of the filtration efficiency does not exhibit any significant shift after 16 hours of machine run. Similar consistency is shown in the value of the basis weight of the nanofiber layer, shown in Figure 9.

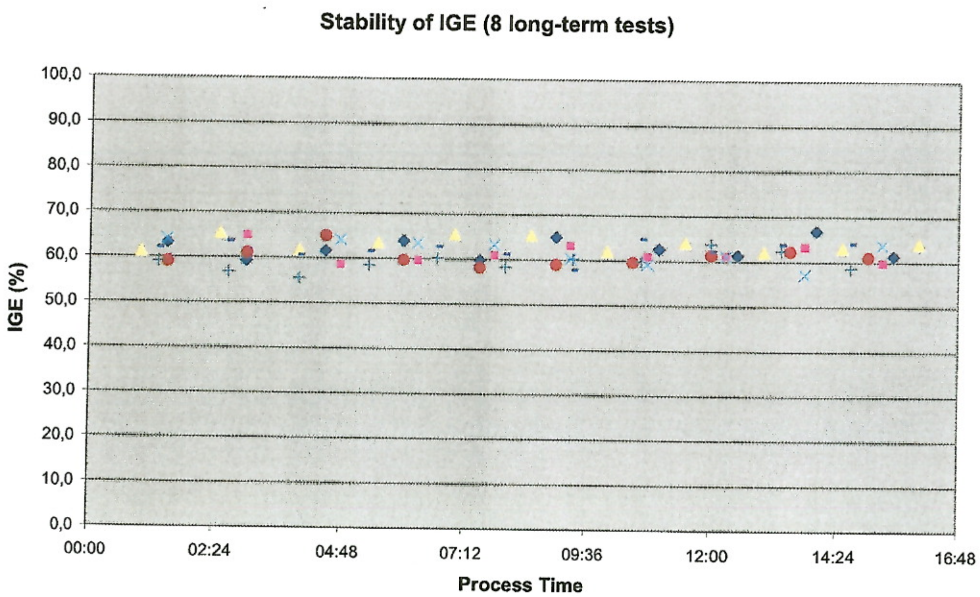


Figure 8. Stability of initial gravimetric filtration efficiency of the media produced at the industrial nozzle-less electrospinning equipment

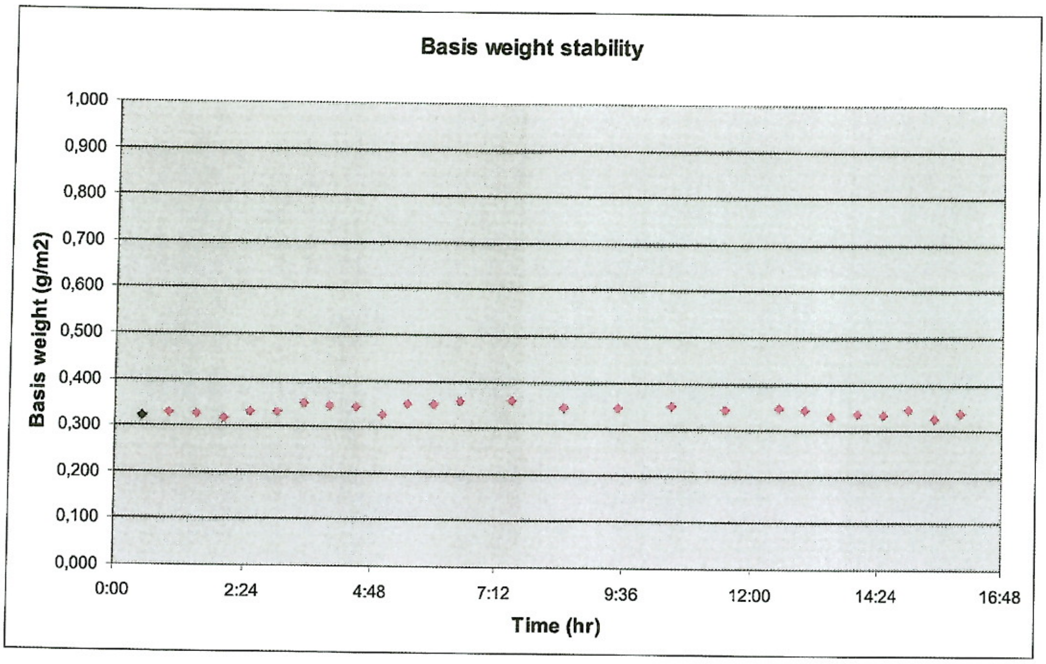


Figure 9. Consistency of nanofiber layer basis weight produced with industrial nozzle-less electrospinning equipment

The third important parameter of the filtration media is its homogeneity across the width of the roll. The data for the 1.6 meter wide roll produced with the machine in Figure 6 are shown in the graph in Figure 10. Pressure drop was measured in 10 evenly distributed points at a cross section of the substrate belt.

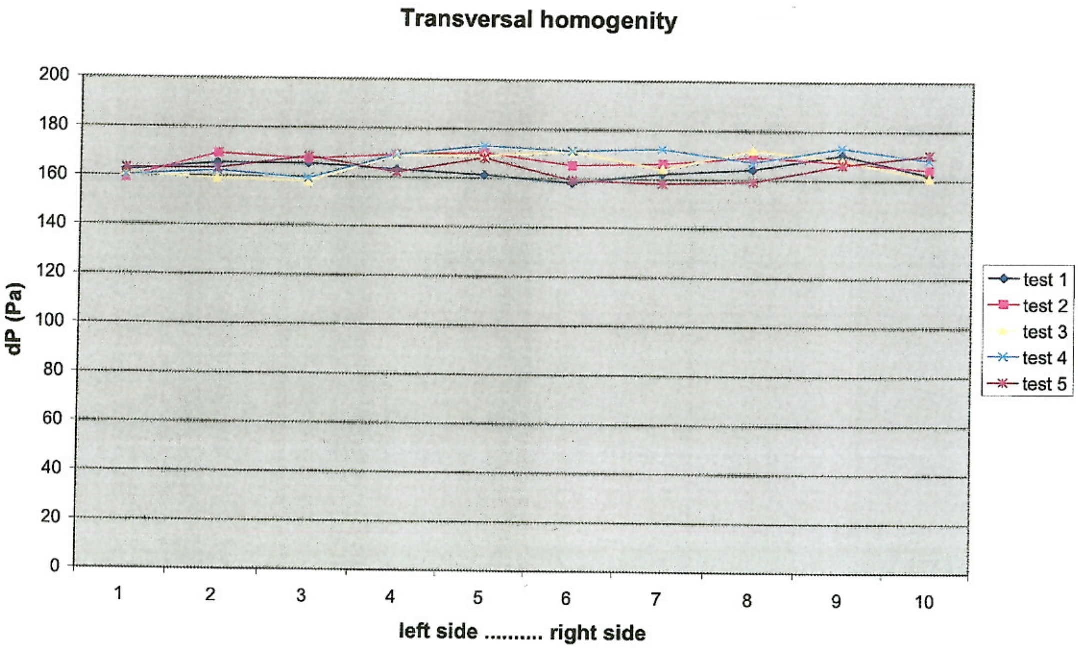


Figure 10. Transversal homogeneity of the filtration media (1.6 m width, dP = pressure drop)

Production capacity of the industrial electrospinning line for Polyamide 6 is illustrated in Figure 11.

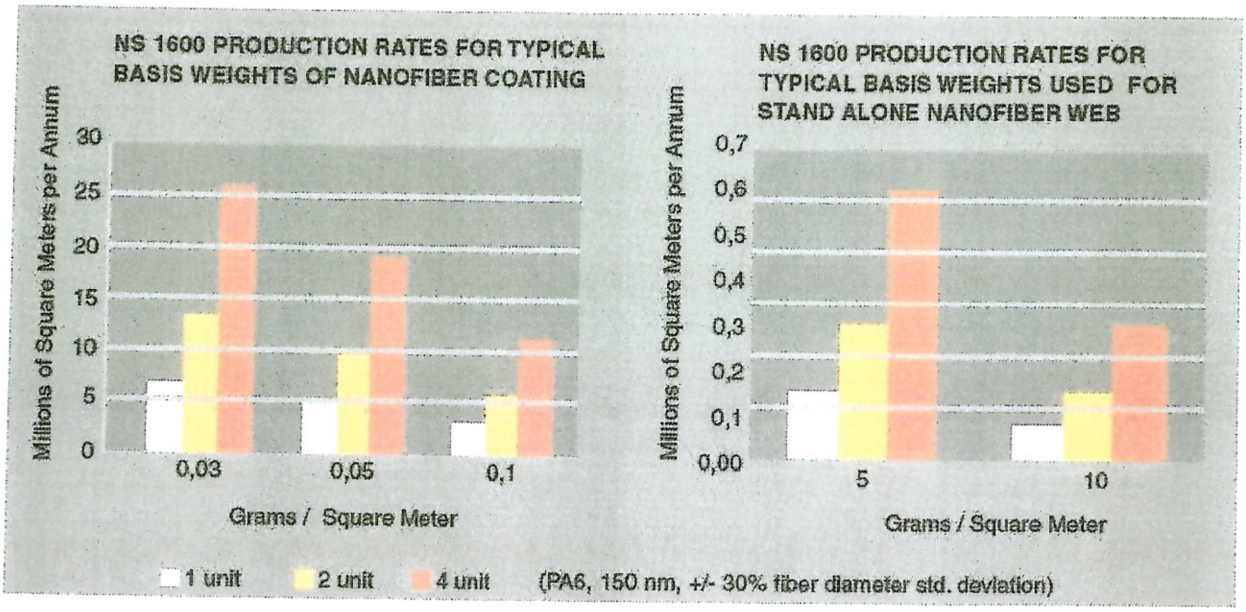


Figure 11. Production capacity of the nozzle-less electrospinning line with Polyamide 6

CONCLUSION

High-quality low-cost production of nanofiber layers is essential to support the enormous amount of research results being obtained at many universities and research centers. The described nozzle-less electrospinning technology has matured to a level where large scale production use is common, and can be modified for practically all known polymers soluble in organic solvents and water, as well as for polymer melts. This opens commercial opportunities for hundreds of ideas developed in the academic sphere.

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2.2. Publikace 2:

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Samostatná kapitola v monografii.

Přínos uchazeče:

Analýza a porovnání teoretických modelů elektrostatického zvlákňování (tvorba nanovláken, beztryskový přístup) v kontextu technologie v průmyslovém měřítku. Kritické porovnání alternativních způsobů výroby nanovláken. Metodické vedení průmyslových experimentů, sběr a vyhodnocení experimentálních výsledků, vyhodnocení parametrů technologie Nanospider (rovnoměrnost výroby a produktových vlastností filtračních materiálů s nanovlákennou vrstvou).

Proprietary Nanofiber Technologies and Scale-Up

Stanislav Petrík

Abstract An overview of scalable methods for industrial production of nanofibers is given. The theoretical principles of both nozzle- and nozzle-less electrospinning processes are discussed. Productivity limits of electrospinning and competing/ complementary technologies (nano-meltblown, force-spinning, islets-in-the sea), together with their predominant potential application areas, are described. Newest developments in production methods for nanofibers are introduced, e.g. nozzle-less co-axial electrospinning and single-nanofiber preparation.

Keywords Nanofibers · Electrospinning · Co-axial · Nozzle-less · Drug delivery · Bio-medical · Force spinning · Nanofiber production

Abbreviations

Φ	Scalar velocity potential
p	Hydrostatic pressure
ρ	Liquid density
E_0	Electric field strength
γ	Surface tension
ω	Angular frequency
k	Wave number
E_c	Critical electric field intensity
λ	Spatial period ("wavelength")
a	Capillary length

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1 Introduction

Nanofibers attract consistently growing attention for many applications, including bio-medical, since recent decade. Unique morphology of nanofibers, their extremely high surface area, material variability and relatively simple methods for their preparation opened huge field for both technology processes and material applications research. Number of publications related to the use of nanofibers as delivery systems exhibit probably the highest growth during last few years (Yu et al. 2009).

Electrospinning as a method for production of very fine (submicron) fibers has developed into a dominant technology of industrial production scale. Some limitations connected with the use of (often dangerous) solvents and relatively low productivity for some applications motivate developments of alternate methods which are being commercialized during recent years.

Electrospinning methods for creating nanofibers from polymer solutions have been known for decades (Kirichenko et al. 2007; Ramakrishna et al. 2005). The nozzle-less (free liquid surface) technology opened new economically viable possibilities to produce nanofiber layers in a mass industrial scale, and was developed in the past decade (Jirsak et al. 2005; Petrik and Maly 2009). Hundreds of laboratories are currently active in the research of electrospinning process, nanofiber materials, and their applications. Nanofiber nonwoven-structured layers are ideal for creating novel composite materials by combining them with usual nonwovens. The most developed application of this kind of materials is air filtration (Jaroszczyk et al. 2009). Liquid filters and separators are being developed intensively with very encouraging results. Inorganic/ceramic nanofibers attract growing interest as materials for energy generation and storage (solar and fuel cells, batteries), and catalytic materials (Kavan and Grätzel 2002; Rubacek and Duchoslav 2008; Bognitzki et al. 2001).

To fully explore the extraordinary number of application opportunities of nanofibers, the availability of reliable industrial-level production technology is essential. This chapter intends to demonstrate that some of the technologies have matured to this stage.

2 Nanofibers as Delivery Systems

Well known are several bio-medical applications utilizing nanofiber materials, often from biocompatible/degradable polymers like PLA, gelatine, collagen, chitosan. These developing applications include wound care, skin-, vessel-, bone-scaffolds, drug delivery systems and many others (Proceedings 2009).

One of the first reports about electrospinning nanofibers as delivery systems was published by Kenawy et al. (2002) Electrospun fiber mats were explored as drug delivery vehicles using tetracy-cline hydrochloride as a model drug. The mats were made either from poly (lactic acid) (PLA), poly (ethyl-ene-co-vinyl acetate)

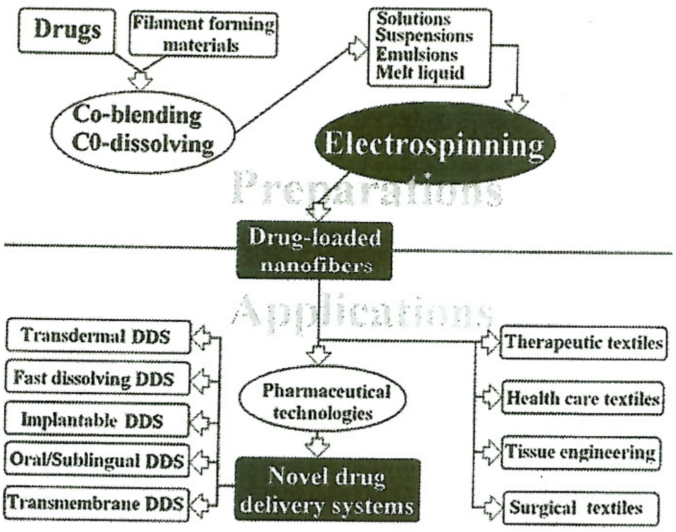

Fig. 1 Applications and preparations of electrospun drug-loaded nanofibers (Yu et al. 2009) (Courtesy of Scientific Research Publishing)

(PEVA), or from a 50:50 blend of the two from chloroform solutions. A detailed overview of delivery bio-medical applications of nanofibers was published by Yu et al. (2009). Their schematic diagram (Fig. 1) illustrates most of the opportunities the nanofiber systems offer for drug delivery, scaffold/tissue engineering, health care textiles, surgical textiles, and other systems.

The active agents (i.e. drugs) can be incorporated into nanofibers in several ways. The most common one used to be to mix functional particles into the polymer solution the nanofiber material is being prepared from. This approach often limits technological processability of the material. As many authors have proven (Buzgo et al. 2013; Mickova et al. 2012; Williams et al. 2012), co-axial (core-shell) nanofibers offer much larger potential as delivery systems, because of their capability to incorporate and protect also the agents which are not spinnable or non-dispersable in homogeneous nanofibers. Besides „trivial"technological approach based on co-axial needle electrospinning (i.e. Azarbayjani et al. (2010)), Lukas'group at the Technical University of Liberec (Vyslouzilova et al. 2010) has patented and published a nozzle-less productive electrospinning device described below.

3 Electrospinning

The electrospinning process is an interesting and well-characterized physical phenomenon and has been an attractive subject for theoretical investigations of several groups (Bognitzki et al. 2001; Doshi and Reneker 1995; Thompson et al. 2007;

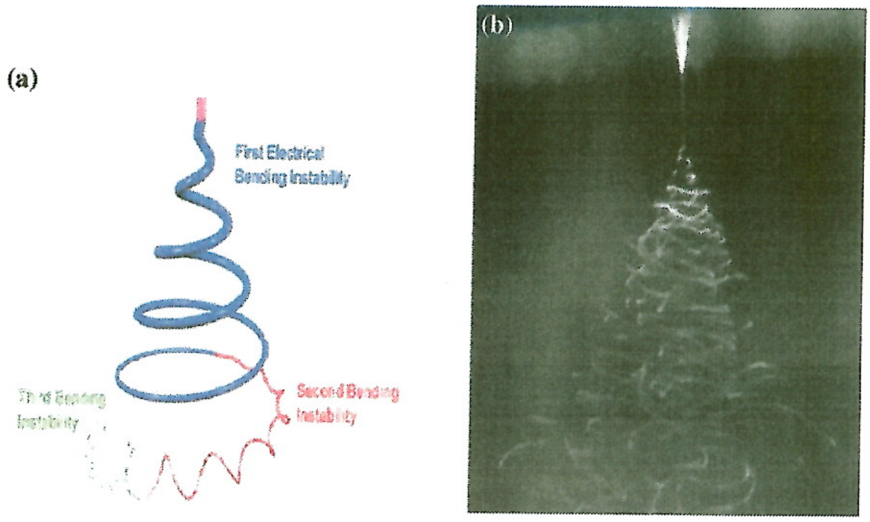

Fig. 2 The path of an electrospinning jet **a** schematic, **b** stroboscopic photograph (*Courtesy of Darrell Reneker, University of Akron*)

Shin et al. 2001; Yu et al. 2006; Hohman et al. 2001). Most work concentrates on the essentials of the process—the nanofiber formation from a liquid polymer jet in a (longitudinal) electric field. It has been theoretically described and experimentally proven that the dominant mechanism is whipping elongation occurring due to bending instability (Thompson et al. 2007; Yu et al. 2006; Hohman et al. 2001). Secondary splitting of the liquid polymer streams can occur also (Kirichenko et al. 2007), but the final thinning process is elongation.

In Fig. 2, the schematic of bending mechanism derived from physical model (a) is compared with a stroboscopic snapshot (b) (Reneker 2009).

A comprehensive analysis (electrohydrodynamic model) of the fiber formation mechanisms published by (Hohman et al. 2001) describes the regions of individual kinds of instability observed during the process. It has predicted and experimentally proven that there is a domain of the process variables where bending instability dominates, as illustrated in Fig. 3.

The efforts to scale up the electrospinning technology to an industrial production level used to be based on multiplication of the jets using multi-nozzle constructions (Kirichenko et al. 2007).

In Fig. 4, the multi-nozzle spinning head developed by NanoStatics Company is shown. The principle is based on an idea to feed multiple nozzles from a single source of the polymer solution.

Figure 5 shows the multi-nozzle spinning part of the machine being commercialized by TOPTEC Company. The device uses upwards direction of electrospinning in order to eliminate polymer droplets eventually falling from conventional down-oriented electrospinning elements.

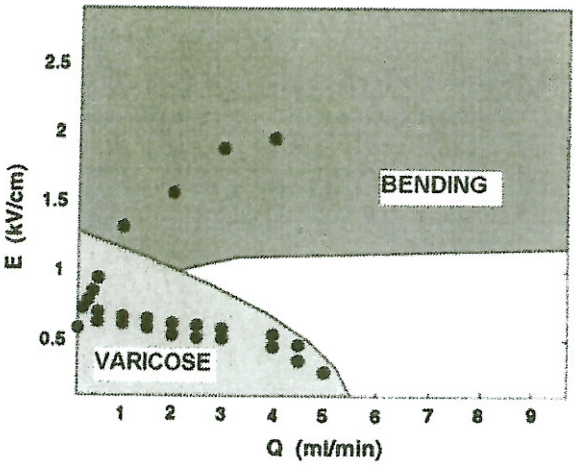

Fig. 3 Operating diagram for a PEO jet. The *upper shaded* region shows the onset of the whipping instability, the *lower* one shows the onset of the varicose instability (Hohman et al. 2001b)

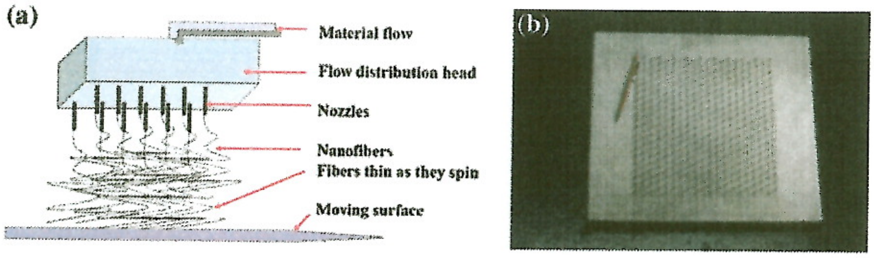

Fig. 4 Schematic (**a**), and photograph (**b**) of a multi-nozzle spinning head by NanoStatics (NanoStatics 2007)

However, the number of jets needed to reach economically acceptable productivity is very high, typically thousands. This brings into play many challenging task, generally related to reliability, quality consistency, and machine maintenance (especially cleaning). The nozzle-less electrospinning solves most of these problems due to its mechanical simplicity, however, the process itself is more complex because of its spontaneous multi-jet nature. The study by (Lukas et al. 2008) focused on the process of multi-jet generation from a free liquid surface in an electric field. They derived an expression for the critical spatial period ("wavelength")—the average distance between individual jets emerging from the liquid surface (Fig. 5). In this system, self-organization of the jets occurs, thus the number and spacing of the jets is optimal even if the technology variables (voltage, viscosity and surface tension of the solution) change. This feature leads to significant improvement of the process stability and consistent quality of the produced nanofiber layer.

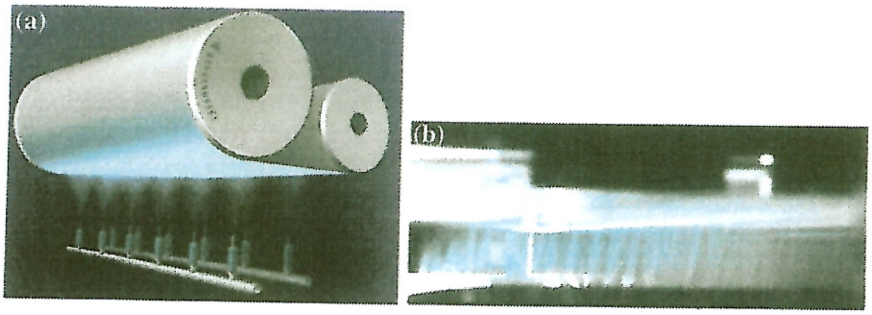

Fig. 5 Schematic (**a**), and photograph (**b**) of a multi-nozzle spinning head by TOPTEC (TOPTEC 2011)

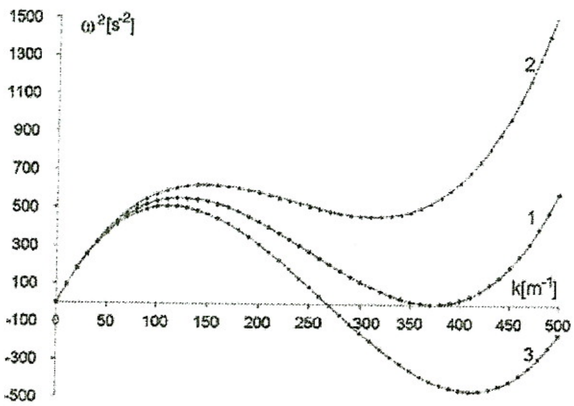

Fig. 6 Relationship between the square of the angular frequency and the wave number for distilled water, electric field is the parameter *1* $E = E_c = 2.461\ 945\ 094 \times 10^6$ V/m, *2* $E = 2.4 \times 10^6$ V/m, and *3* $E = 2.5 \times 10^6$ V/m (Lukas et al. 2008) (Courtesy of D. Lukas, TU Liberec)

The study showed that the process can be analyzed using Euler's equations for liquid surface waves

$$\nabla\left(\rho\frac{\partial\Phi}{\partial t}+p\right)=0 \tag{1}$$

where Φ is the scalar velocity potential, p is the hydrostatic pressure, and ρ is the liquid density. They derived the dispersion law for the waves in the form

$$\omega^2=\left(\rho g+\gamma k^2-\varepsilon E_0^2 k\right)\frac{k}{\rho} \tag{2}$$

where E_0 is electric field strength, γ—surface tension.

The relationship between angular frequency ω and wave number k is in Fig. 6, electric field is the parameter. When a critical electric field intensity is reached (E_c, curve 1), ω^2 is turned to be negative, ω is then a purely imaginary value, and hence, the amplitude of the liquid surface wave

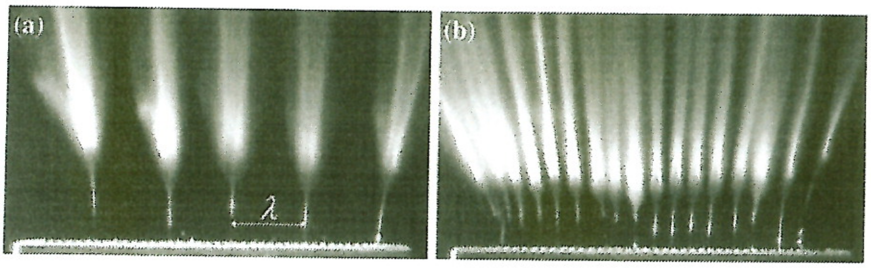

Fig. 7 **a** Free liquid surface electrospinning of Polyvinyalcohol at 32 kV, and **b** 43 kV (*Courtesy of David Lukas, Technical University of Liberec*)

$$\xi = Ae^{qt}\exp(ikx) \quad (3)$$

exponentially grows, which leads to an instability.

Critical field strength can then be expressed

$$E_c = \sqrt[4]{4\gamma\rho g/\varepsilon^2} \quad (4)$$

From this equation, they derived the expression for the critical spatial period ("wavelength")—the average distance between individual jets emerging from the liquid surface (Fig. 7).

$$\lambda_c = 2\pi/k_c = 2\pi a \quad (5)$$

and

$$\lambda = 12\pi\gamma/\left[2\varepsilon E_0^2 + \sqrt{\left(2\varepsilon E_0^2\right)^2 - 12\gamma\rho g}\right] \quad (6)$$

a is the capillary length

$$a = \sqrt{\gamma/\rho g} \quad (7)$$

The simplest realization of the nozzle-less electrospinning head is in Fig. 8a. A rotating drum is dipped into a bath of liquid polymer. The thin layer of polymer is carried on the drum surface and exposed to a high voltage electric field. If the voltage exceeds the critical value, a number of electrospinning jets are generated. One of the main advantages of nozzle-less electrospinning is that the number and location of the jets is set up naturally in their optimal positions. In the case of multi-needle spinning heads, the jet distribution is made artificially. The mismatch between "natural" jet distribution and the real mechanical structure leads to instabilities in the process, and to the production of nanofiber layers which are not homogenous.

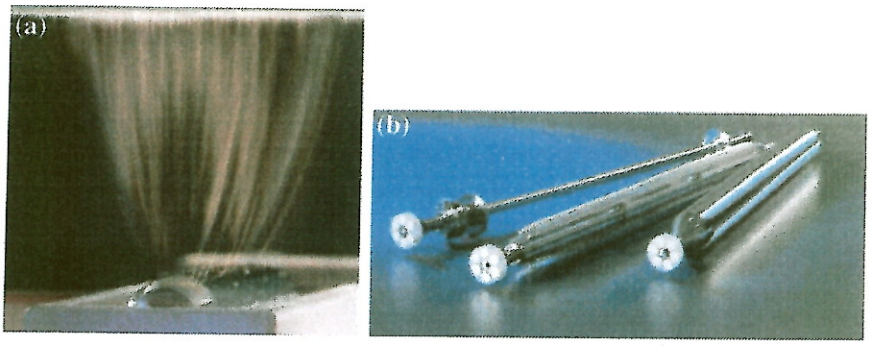

Fig. 8 **a** Free liquid surface electrospinning from a rotating electrode, and **b** various types of spinning electrodes

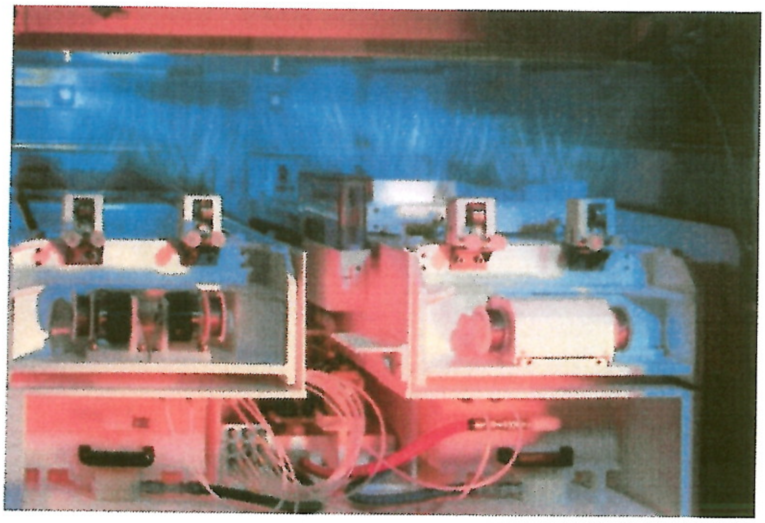

Fig. 9 Photograph of production electrospinning heads inside Nanospider™ machine (2nd generation). Four strings with upwards fiber jets. (Elmarco 2013)

Several types of rotating electrodes for free liquid surface electrospinning for industrial machines have been developed (Fig. 8b). However, the drum type is still one of the most productive.

Recent significant improvement of the production nozzle-less electrospinning equipment, commercially available from Elmarco Company, is illustrated in Figs. 9 and 10. The system uses stationary string electrodes supplied with polymer solution by a proprietary moving "painting" head. This led to a dramatic decrease of solvent evaporation during the process which has to be removed from the exhaust air released from the machine. Also, the polymer solution concentration is stable, enabling to continuously run the production process for long time, typically more than 24 hours.

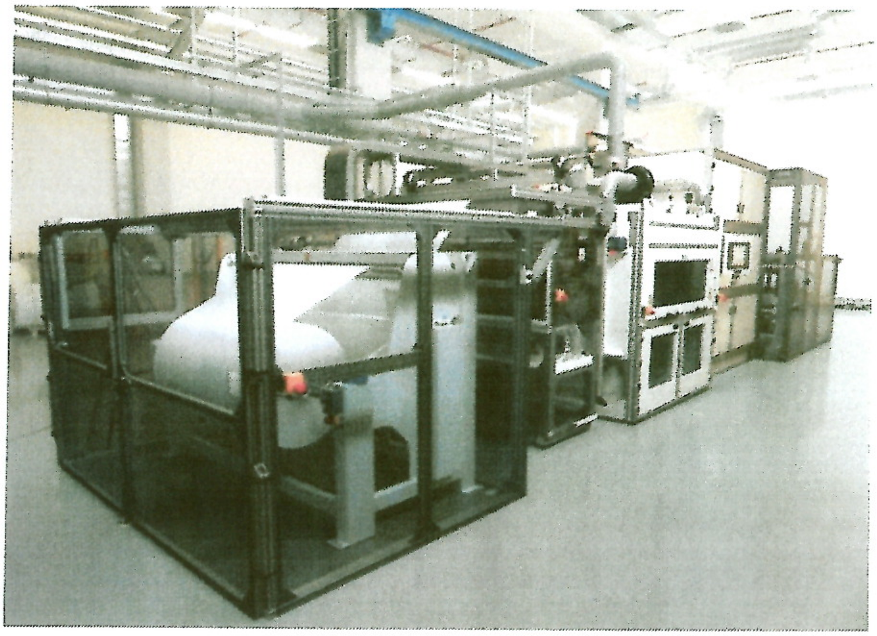

Fig. 10 Nanospider^{TM} production line NS 8S1600U by Elmarco (2013)

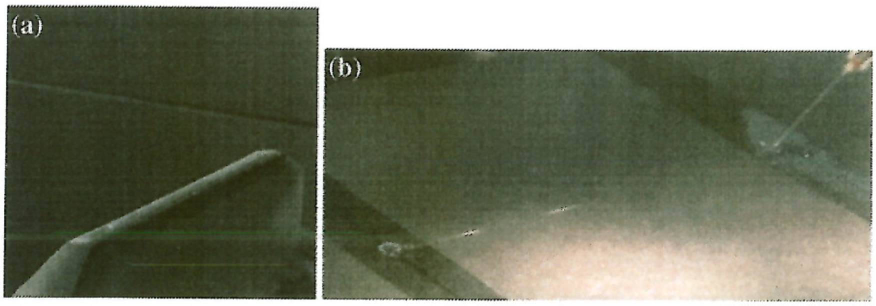

Fig. 11 Co-axial nozzle-less spinning head (**a**), single nanofiber drawing (**b**) (*Courtesy of D. Lukas, TU Liberec*)

For many applications, especially bio-medical, the co-axial (core-shell) nanofibers attract intense research interest recently. A single-needle laboratory apparatus can be relatively simple, however, a more productive equipment development is challenging. The researchers at the Technical University of Liberec (Czech Republic) successfully demonstrated the nozzle-less co-axial electrospinning head (Fig. 11) possessing the same advantages as Nanospider^{TM} (Vyslouzilova et al. 2010). The same team works on development of a single-nanofiber production

Table 1 Comparison of nozzle versus Nozzle-less electrospinning

Production variable	Nozzle	Nozzle-less
Mechanism	Needle forces polymer downwards. Drips and issues deposited in web	Polymer is held in bath, even distribution is maintained on electrode via rotation
Hydrostatic pressure	Production variable–required to be kept level across all needles in process	None
Voltage	5–20 kV	30–120 kV
Taylor cone separation	Defined mechanically by needle distances	Nature self-optimizes distance between Taylor cones
Polymer concentration	Often 10 % of solution	Often 20 % or more of solution
Fiber diameters	80, 100, 150, 200, 250 and higher. Standard deviation likely to vary over fiber length	80, 100, 150, 200, 250 and higher. Standard deviation of ±30 %

system, which could provide unique nanofiber structures for special low-volume applications, e.g. sensors (Tsai et al. 2011). Advantages and disadvantages of nozzle and nozzle-less production are summarized in Table 1.

4 Alternate Technologies for Nanofibers

Research and development centers are very active in their efforts to further improve productivity of the manufacturing process. Novel methods for the production of sub-micron fibers are being developed. The individual methods can be considered to be complementary rather than competing. This is especially true with respect to the fiber diameter distribution and fiber layer uniformity.

Figure 12 shows the **extrusion methods** being developed by Hills Inc. (HILLS Inc 2011). Dominant technique that Hills practices to produce nanofibers is done using the Island-In-The-Sea (fibers within fibers) method. This method has the capability of making a large number of fibers within a fiber. The Hills declare they are able to spin up to 1,200 fibers within a single fiber. Using the same techniques, these filament can be produced as hollow tubes.

Centrifugal forces for elongation of liquid polymer into thin fibers are used in the approach developed by (Dauner et al. 2008), illustrated in Fig. 13. The productivity of the process they claim is high (up to 1,000 cm^3/m h), however, the fiber diameter distribution and homogeneity of the deposited nanofiber layer is not at the levels achieved by electrospinning.

Strong commercialization effort is shown recently by FibeRio Company (www.fiberio.com), developing so called "force spinning" principle into an industrial scale. The principle discovered at the University of Texas Pan American is based on high-speed rotating spinneret depositing nanofibers on the radial collector (Fig. 14)

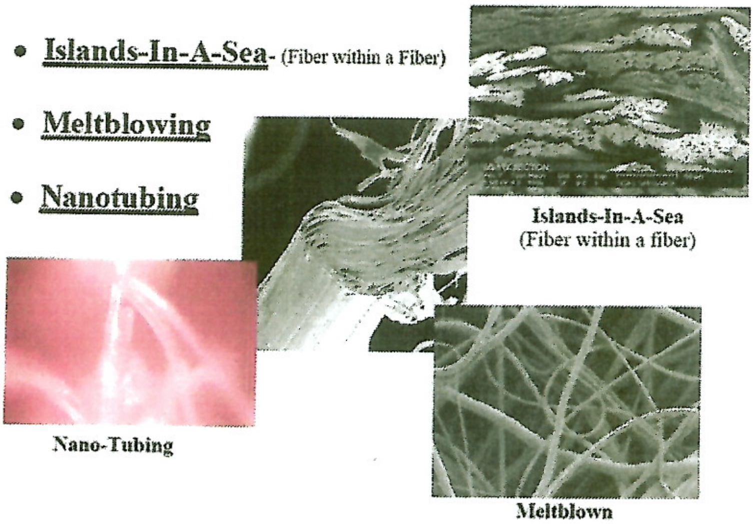

Fig. 12 Fibers made by extrusion methods (HILLS Inc 2011) (Courtesy of HILLS Inc.)

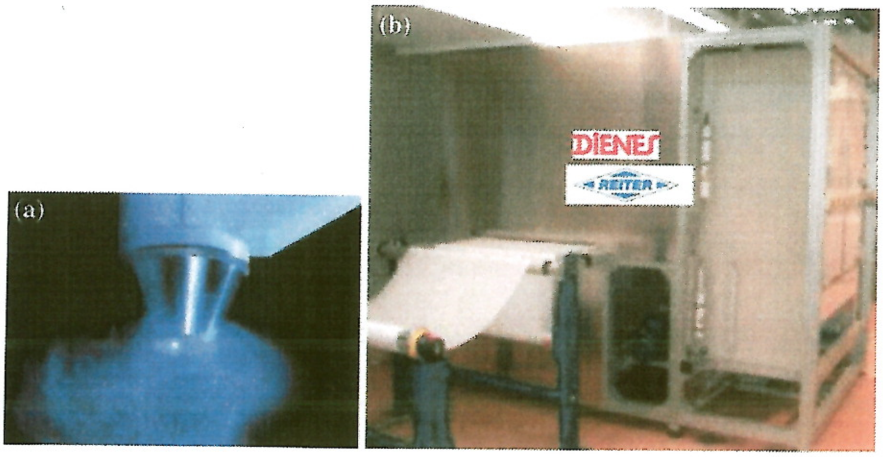

Fig. 13 Centrifugal spinning head (**a**) and a pilot production line by Dienes/Reiter (**b**) (Dauner et al. 2008)

(FibeRio 2013). The productivity of the process should be an order higher compared to electrospinning. However, mechanical design of the equipment is much more demanding (rotating parts at tens of thousands rpm, fed with liquid polymer). Also, radial deposition of the produced nanofiber materials could be challenging task for the applications, where continuous roll-to-roll deposition of thin layer to a substrate is required, e.g. at the nanofiber filtration media production.

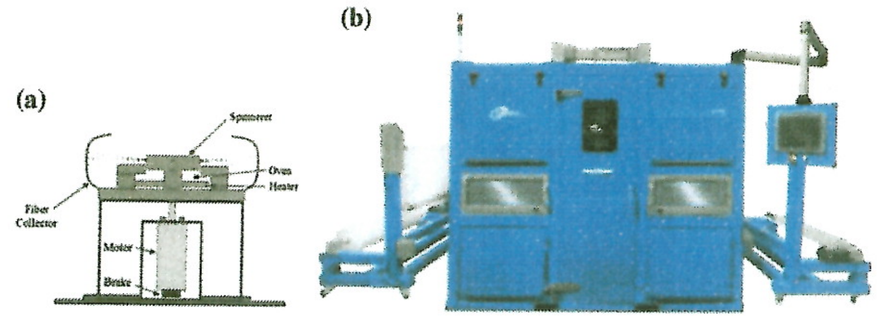

Fig. 14 Force Spinning™ technology by FibeRio: Schematic of the machine design (**a**), and photograph of the Fiber Engine® FS1000 production line (**b**) (FibeRio 2013)

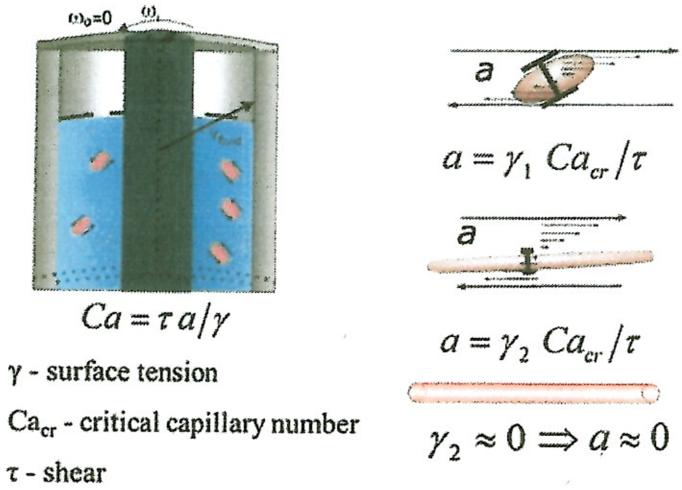

Fig. 15 Liquid shear nanofiber fabrication process (NCSU 2013)

Shear forces in a rotating liquid containing polymer droplets are the basis of XanoShear™ method developed at North Carolina State University (Alargova et al. 2004). The method is being commercialized by Xanofi Company (www.xanofi.com), offering to the market several nanofiber materials (filtration media, cell scaffolds, acoustic absorbents, etc.). Schematic of the equipment is in Fig. 15. Liquid shear nanofabrication process is a novel method to prepare nanofibers by subjecting polymer solution droplets to simultaneous shear and anti-solvent induced precipitation in viscous liquid media. The typical lab scale process involves creation of laminar shear in viscous media (glycerol + antisolvent) using a shear impeller and injection of polymer solution droplets into it. During shear process, the low interfacial tension between major component of viscous media i.e.

glycerol and polymer solution, leads to infinite stretching of polymer droplets into proto fibers and simultaneous precipitation by anti-solvent component in viscous media gives rise to solidified fibers of very thin diameter in the range 300–500 nm.

5 Conclusion

Individual production methods for nanofiber materials will likely find different areas of application. More productive extrusion technologies compromise fiber diameter and homogeneity and will likely be used in production cost sensitive applications like hygiene nonwovens, while high quality electrospinning technologies will be used in products where their high added value and need for low amounts of the material can be easily implemented (air and liquid filtration, biomedicine)..

High-quality low-cost production of nanofiber layers is essential to support the enormous amount of research results being obtained at many universities and research centers. Some of the technologies (nozzle-less electrospinning, force spinning, nano-meltblown) have matured to a level where large scale production use is common, and can be modified for practically all known polymers soluble in organic solvents and water, as well as for polymer melts. This opens commercial opportunities for hundreds of ideas developed in the academic sphere.

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3. Filtrace vzduchu – nejrozšířenější komerční aplikace nanovlákenných materiálů

Filtrační průmysl je přirozeným primárním trhem pro technologie vyrábějící nanovlákna. Přínosy zmenšování průměru vláken filtračního média jsou známé desítky let. Základní výhoda nanovláken spočívá ve změně mechanizmu filtrace, která přináší výrazné zvýšení filtrační účinnosti při pouze nepatrném zvýšení tlakového spádu (resp. snížení permeability).

První publikace uvedená v této části habilitační práce (*Publikace 3*) se zabývá vztahy mezi středním průměrem nanovláken ve filtrační vrstvě, jejich celkovou hmotností (tzv. plošnou hmotností, vyjádřenou nejčastěji v g/m^2) a filtračními vlastnostmi výsledného materiálu. Původním výsledkem je zavedení pojmu tzv. „relativní délky vlákna“, které je možno vyjádřit například v km/m^2 (střední celková délka vlákna naneseného na 1 m^2 filtračního média). Experimentální výsledky publikované v práci ukazují, že pro prakticky používaný rozsah průměrů nanovláken má relativní délka vlákna mnohem větší vliv na filtrační vlastnosti výsledného materiálu, než do této doby tradičně používaná plošná hmotnost. Produktový přístup k průmyslové výrobě filtračních materiálů s nanovlákny tak znamenal zásadní změnu v řízení procesu výroby filtračních médií.

Další publikace uvedená v habilitační práci (*Publikace 4*) je výsledkem spolupráce uchazeče a jím vedeného týmu s firmu Cummins Filtration v oblasti filtračních aplikací nanovlákenných materiálů pro náročné podmínky v těžkých motorech (především dieselových) používaných například v lodní dopravě nebo v záložních zdrojích energie. V článku jsou ilustrovány přínosy nanovlákenných materiálů na konkrétních konstrukcích vzduchových filtrů pro tuto oblast. Nejvýznamnější přínosy spočívají ve zvýšení filtrační účinnosti a čistitelnosti filtrů.

Třetí publikace (*Publikace 5*) v této části habilitační práce se zabývá poměrně úzkou (ale velmi významnou) snahou rozšířit proces beztryskového elektrostatického zvlákňování i na chemicky velmi těžko rozpustné polymery – polyoelefiny, které se průmyslově zpracovávají tavením. Publikovány jsou výsledky experimentů na novém laboratorním stroji, který pracuje s taveninou namísto roztoku. Úspěšné dotažení tohoto přístupu do průmyslového stadia bude znamenat významné rozšíření použitelnosti této technologie. Výsledky publikace ukazují, že takové strojní zařízení je reálné, ale kompletní vyřešení technologie si vyžádá další výzkum v oblasti polymerů.

3.1. Publikace 3:

Petrík,S. - Malý,M. - Rubáček,L.: **Design and Parameters of Cellulose Filter Media with Polymer Nanofiber Layer.** In: Technical Proceedings of the NANOTECH 2008 Symposium, Boston, June 1-5, 2008, pp. 329 – 332 (ISBN 978-1-4200-8511-2).

Oponovaný článek ve sborníku symposia NANOTECH 2008, Boston, June 1-5, 2008.

Přínos uchazeče:

Článek je jedním z prvních příspěvků uchazeče k problematice vzduchové filtrace s využitím tenké nanovlákenné vrstvy na povrhu tradičního filtračního média. Uvádí původní výsledky výzkumu závislosti filtračních vlastností materiálů na distribuci průměrů nanovláken, morfologii a celkové plošné hmotnosti nanovlákenné vrstvy. Tento výsledek znamenal zásadní změnu chápání pojmu „výkon" výrobního procesu, který byl do té doby hodnocen spíše kvantitativně ve smyslu celkové hmotnosti vyprodukovaných vláken. Zavedení pojmu „relativní délky vlákna" („relative fiber length") umožnilo porovnávání nanovlákenných filtračních médií na základě jejich skutečných produktových parametrů, tzn. filtrační účinnosti a tlakového spádu. Uchazeč vypracoval metodiku hodnocení a porovnávání nanovlákenných filtračních materiálů, definoval veličinu „relative fiber length", vedl návrh a realizaci experimentů a provedl vyhodnocení a intepretaci výsledků, včetně napsání publikace a prezentace výsledků na několika mezinárodních konferencích.

Design and Parameters of Cellulose Filter Media with Polymer Nanofiber Layer

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ABSTRACT

Nanofiber polymer layer deposited on regular cellulose filter media usually shifts air filtration parameters of this material several classes higher. Very fine nanofiber web of basis weight of 0.01 gsm to 0.1 gsm improves filtration efficiency for submicron particles by hundreds of percent, while lowering air permeability by only tens of percent. This evident benefit becomes to be widely commercially accessible due to the availability of productive industrial-scale Nanospider™ technology.

Influence of morphology of the nanofiber layer (fiber diameter, porosity, fiber shape and orientation) on filtration parameters of the air filtration media has been studied. Preparation method of the filtration media samples and their analysis will be described in the paper. It will be shown that the morphology of nanofiber layer plays usually more important role than its basis weight. Some new physical/geometrical values will be introduced to reflect these relations.

Keywords: nanofiber, air filtration, cellulose media

1 INTRODUCTION

Influence of morphology of the nanofiber layer (fiber diameter, porosity) on filtration parameters of the air filtration media has been studied. All samples analyzed in this paper have been prepared by using an industrial production NanospiderTM machine. Preparation method of the filtration media samples and their analysis are described in the paper. It has been shown that the morphology of nanofiber layer plays usually more important role than its basis weight. Some new physical/geometrical values are introduced to reflect these relations.

Nanofiber polymer layer deposited on regular cellulose filter media usually shifts air filtration parameters of this material several classes higher. A very fine nanofiber web of basis weight of 0.01 gsm to 0.1 gsm improves the filtration efficiency for submicron particles by hundreds of percent, while lowering the air permeability by only tens of percent. This evident benefit becomes to be widely commercially accessible due to the availability of productive industrial-scale NanospiderTM technology [1].

Usual parameter discussed (and required) by nanofiber filtration media users is the basis weight of the nanofiber layer. However, experience with final (product) parameters of filters shows, that there is not a very strong correlation between basis weight, filtration efficiency and permeability (or pressure drop), at least in the case of cellulose substrate combined with relatively low-weight polymer nanofiber layer.

Mechanism of filtration process on fibrous media has been discussed in several publications [2-6]. For example, for cellulose filtration media of solidity ß in the range of 0.11-0.33 and an average pore diameter of 12-84 µm, it has been shown that pressure drop depends on fiber diameter df according to relation [2]:

$$\Delta p = \frac{\mu \cdot v \cdot w_b \cdot h}{d_f^2 \cdot \rho_f \cdot (-0{,}984 \cdot \ln \beta - 0{,}47)} \qquad (1)$$

where μ is air dynamic viscosity, w_b - media basis weight, h - media thickness, ρ_f - fiber density, β - filter solidity (or packing density) - volume of fibers/volume of filter.

However, in the case of low basis weight nanofiber layer, where molecular (or transition) flow regime takes place, following equation is considered to be valid [5]:

$$\Delta p = \frac{\mu \cdot v \cdot w_b \cdot h}{r_f \cdot \lambda} \qquad (2)$$

where r_f is radius of nanofiber and λ means free path of molecules.

Hence, the combination of cellulose medium with polymer nanofiber layer will require more complex models to describe behaviour of the final filtration material. Systematic experimental study of correlations between final product parameters (filtration efficiency, pressure drop) and morphology of cellulose/nanofiber media can provide useful data for both theoretical understanding of filtration mechanisms and practical design of air filters.

2 EXPERIMENTAL

For this study, we prepared 42 samples of controlled basis weight and fiber diameters (6 series, 7 samples in each). Nanospider production machine has been used, as it provides good long-term consistency of filtration media parameters (16 hours run with repeatability in the range of ±5%).

To obtain various basis weights, substrate speed had been varied from 0.2 m/min to 4 m/min for each series of samples, while polymer solution parameters (concentration, etc.) together with electric field intensity determined the range of nanofiber diameter. Nanofiber diameter distribution has been measured by using scanning electron microscope (SEM). Basis weights were obtained either directly by using analytical balances Mettler (higher values) or by extrapolation from its known dependence on substrate velocity (lower ones). Pressure drop and initial gravimetric filtration efficiency have been chosen as representatives of product parameters. They were measured according to EN 779 using NaCl aerosol at following settings: air flow speed: 5 m/min, sample area 100 cm2, flow rate 50 l/min.

3 RESULTS AND DISCUSSION

Fig. 1 illustrates very good correlation between initial gravimetric filtration efficiency and pressure drop, regardless of nanofiber layer parameters (df, wb). As pressure drop monitoring can be relatively easily incorporated into the nanofiber production line, it can be used as a very good parameter for the on-line quality control of final filtration media.

Samples in Fig. 2 show how different nanofiber layers can exhibit similar filtration properties. The first sample is made of thin nanofibers (around 80 nm) and lower basis weight (0.03 gm-2), while the second one is characterized by almost 2-times thicker fibers (144 nm) and more than 3-times higher basis weight (0.10 gm-2).

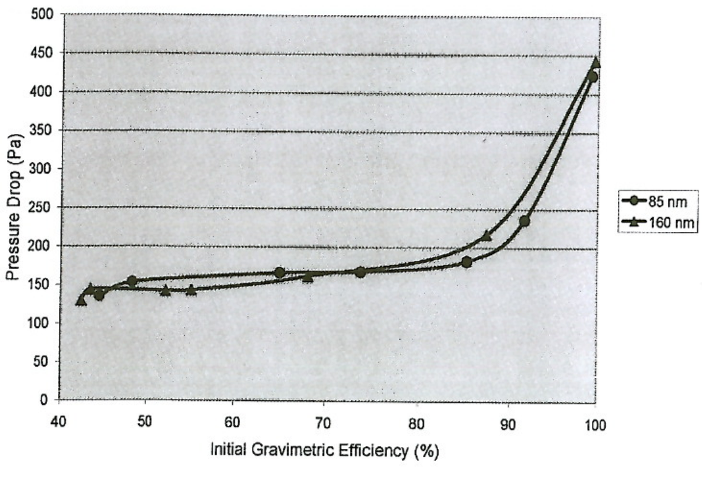


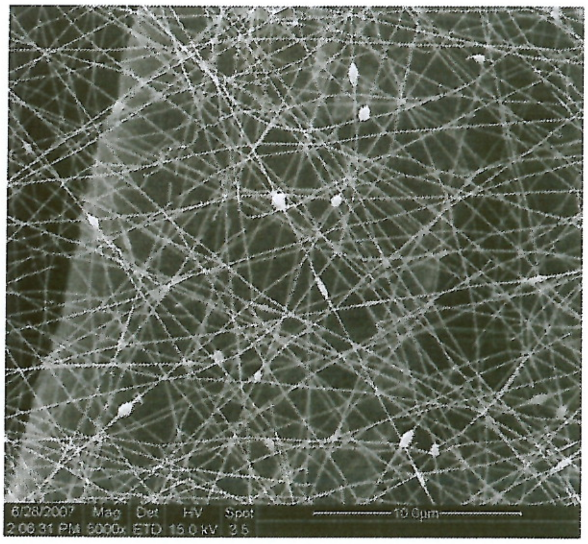
Fig. 1

To consider the influence of both basis weight and fiber diameter on final product filtration parameters, we can define a simple value (Relative Fiber Length Lf) expressing the total length of nanofibers (in kilometers) deposited on unit surface of filtration medium (in square meters):

$$L_f = \frac{w_b}{\pi \cdot \rho \cdot \left(\frac{d_f}{2} \right)^2} \quad (3)$$

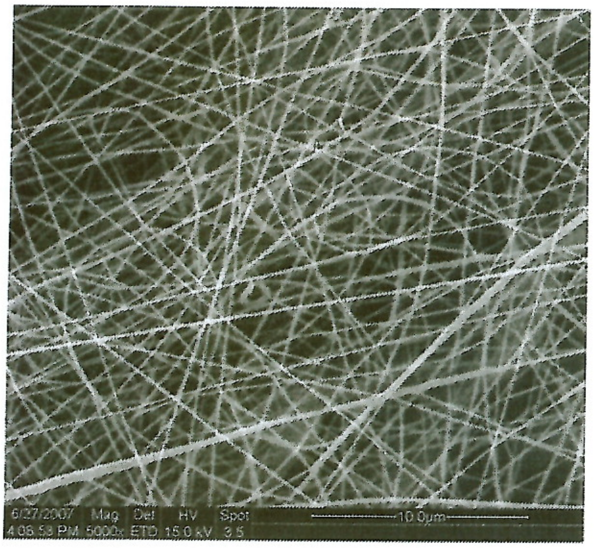
where ρ is density of material of nanofibers.

As it can be seen from the graphs in Fig. 3, both filtration efficiency and pressure drop are in much better correlation with Relative Fiber Length Lf than with nanofiber layer basis weight (wb).



$IGE = 73 \pm 1$ %
$\Delta p = 168 \pm 5$ Pa
$d_f = 83 \pm 22$ nm

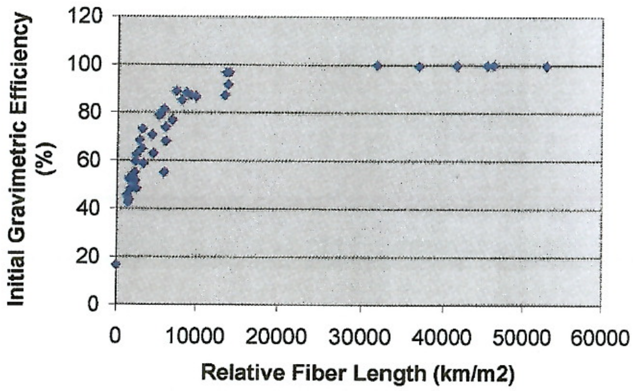
$L_f = 6114$ km.m^{-2}
$w_b = 0.03$ gm^{-2}

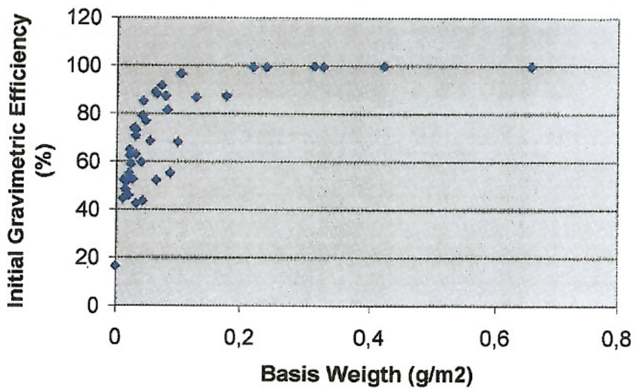


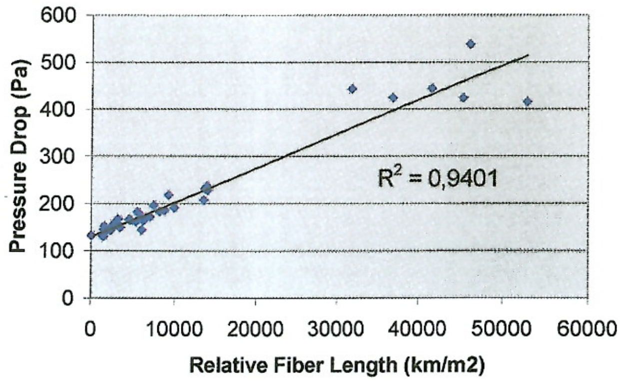
$IGE = 68 \pm 1$ %
$\Delta p = 163 \pm 4$ Pa
$d_f = 144 \pm 36$ nm

$L_f = 6128$ km.m^{-2}
$w_b = 0.10$ gm^{-2}

Fig. 2







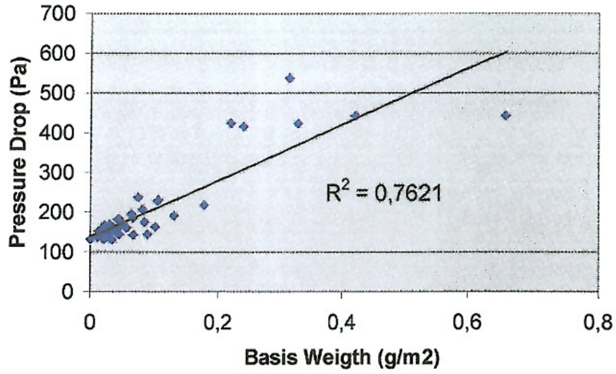


Fig. 3

4 CONCLUSIONS

Experimental results obtained in this study showed that:

- Basis weight of nanofiber layer does not predict filtration parameters well enough. The same initial gravimetric efficiency can be obtained using nanofibers of very different mean diameters, or in other words, of very different basis weights.
- Filtration properties of cellulose media with low-weight polymer nanofibrous layer depend mostly on the total length of nanofibers per media surface unit ("Relative Fiber Length").
- "Relative Fiber Length" is in good correlation with both pressure drop and filtration efficiency.
- Image analysis of SEM pictures can be used for predicting filtration properties of the media.

For more detailed understanding and predicting filtration properties of the media studied here, it will be useful to investigate similar relations using:

- Measurements of fractional filtration efficiency of the samples.
- Observations of the role of dust cake formed on media surface during filter lifetime or in field tests.
- Investigations of the effect of final filter design, pleating of the media, etc.

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3.2. Publikace 4:

Jaroszczyk, T. - Petrik, S. - Donahue, K.: **Recent Development in Heavy Duty Engine Air Filtration and The Role of Nanofiber Filter Media**. Journal of KONES Powertrain and Transport, Vol. 16, No. 4, pp. 207-216. Presented at the International Scientific Congress on Powertrain & Transport Means, Zakopane, Poland, September 13 – 16, 2009 (ISSN 1234-4005).

Oponovaný článek v odborném časopise a sborníku mezinárodního kongresu.

Přínos uchazeče:

Článek uvádí původní výsledky získané v úzké spolupráci s výzkumným oddělením firmy Cummins Filtration. Řeší specifické otázky aplikace nanovlákenných filtračních materiálů v oblasti „Heavy Duty" motorů (lodí, lokomotiv, záložních dieselových elektrocentrál, apod.), včetně dizajnu příslušných filtračních systémů.
Uchazeč vedl výzkum v oblasti technologie přípravy nanovlákenných filtračních materiálů a jejich optimalizace pro uvedenou oblast. Vypracoval metodiku a návrh experimentů, podílel se na zpracování a vyhodnocení výsledků.

RECENT DEVELOPMENT IN HEAVY DUTY ENGINE AIR FILTRATION AND THE ROLE OF NANOFIBER FILTER MEDIA

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Abstract

The development of an engine air filter is based on filter performance requirements, vehicle's operational environment, available space, filter media properties, and production technology. The design process includes analyses of theoretical and empirical models describing filter media performance and aerosol flow in filter housings and through filter elements. Filter media are carefully selected based upon these models and simplified laboratory tests. The filter element design is evaluated in great detail through a series of laboratory and field experiments.

The role of the engine air induction system has increased because of recent engine exhaust particulate and evaporative emission regulations. Engine lifetime, engine emission and fuel consumption depend on the air induction system design and its performance. Providing optimized solutions for these requirements dictates filter development trends. This drives the need for smaller, more compact filters and more efficient filter media with higher permeability. The efficiency can be drastically improved by applying a layer of nanofibers to a cellulose or synthetic substrate. The ISO fractional efficiency test method, that in its final stage of development, can clearly show the advantage of nanofiber filter media. This paper discusses air cleaner design including the newest in-line reduced volume air cleaners and the role of nanofiber filter media in engine air filtration.

Keywords: *engine air induction system, filtration process modeling, filtration mechanisms, filter development process, nanofiber filter media, air filter performance, filter efficiency, dust holding capacity, reentrainment, testing.*

1. Introduction

Major progress in engine air filtration in recent years has been made by introducing in-line; flow-through fluted and pleated filters, and nanofiber filter media. The fluted and

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pleated in-line, reduced-volume filters, provide high filtration performance while occupying less space. In these designs, almost the entire volume of the filter housing accommodates the filter media. The nanofiber filter media offers high efficiency and high permeability. In other words, the efficiency of nanofiber filter media is high at lower flow restriction when compared with traditional cellulose filter media.

Traditional surface type cellulose and surface type synthetic filter media that predominate the engine air filtration market can deliver high dust capacity and high gravimetric efficiency when a dust cake is formed on the media, which takes some time. The initial efficiency and fractional efficiency for fine dust particles of traditional filter media is too low in many applications. Despite this fact, the most commonly used media is still resin-impregnated cellulose paper, because it has low cost and has the ability to pleat into a densely packed pleat block with well-defined pleat shape. However, recent achievements in nanofiber media technology minimize the cost of the media. Knowing that less nanofiber media is needed to construct a filter because of the high media permeability, the nominal cost of the nanofiber media will not increase the overall cost of the filtration system. In fact, the cost may be even lower since smaller filtration systems can be designed for a given flow rate.

The engine air filter market is driven by the following performance requirements for engine air induction systems: low flow restriction, high dust-holding capacity (long life or service-free designs is the main objective in many applications), high gravimetric and fractional efficiency, small, compact components, integrated air intake & silencing system, permanent air intake systems with zero evaporative emissions, exclusive designs, volumetrically efficient filters to fit into available space.

The importance of the engine air induction system has recently increased because of governmental engine exhaust particulate and evaporative emission regulations. Contaminants from the air intake system may significantly contribute to the total engine emissions including crankcase emissions in case of low efficiency filters. According to Schilling [Schilling, 1972], 30% of contaminants penetrating the air induction system and entering the engine passes out the exhaust. In order to reduce the contaminant concentration downstream of the filter, highly efficient filters are needed. High efficiency can be achieved by utilizing nanofiber filter media and proper air intake system design.

Engine operation, lifetime, engine emissions, and fuel consumption depend on the air induction system design and its performance. By integrating the intake and exhaust systems in the new Cummins QSL9, the engine meets EU Stage IIIB and EPA Tier 4 Interim off-highway emission regulations. Moreover, the new system design that was introduced in April 2009, results in efficient combustion that leads to a reduction in fuel consumption by up to 5 percent, dependent on rating [Diesel Progress on Line, August 2009]. The reduced volume Direct Flow filters are 35% smaller then the standard air cleaners.

The objective of this paper is to review the newest engine air induction systems. The focus will be primarily on the design of recently introduced air cleaners and filter media design parameters, their performance and the development trends. In contrast to filters used in industrial applications, ventilation systems, and clean room technology, motor vehicle air filters operate at variable flow rates and flow pulsation experienced frequently in city driving and under variable environmental conditions. The filters are variably loaded with polydisperse dusts at changeable aerosol velocities. The velocity changes can range over an order of magnitude during operation with flow rate of 5 to 5000 m^3/h. The flow rate can be even higher in case of equipment used in the mining industry. The media velocity is in the range of approximately 1 to 200 cm/s. The high end of this range represents prefilters while the range of 0.5 - 25 cm/s is common for pleated main filter elements.

Panel and cylindrical air cleaners still dominate the market. These designs require large housing volumes with relatively small inlets and outlets. Flow turbulences that usually develop in the transition, sudden contraction or sudden expansion areas (Figure 1a), are sources of increased pressure drop. Losses due to turbulent motion of the air increase significantly with increased velocity, because the inertial force is proportional to the velocity squared: $\Delta p = \zeta \bullet \frac{\rho \bullet v^2}{2}$; where ζ = pressure loss coefficient, ρ = air density, v = air velocity. The ζ coefficient is the main contributor to the total pressure drop in a housing with a sudden contraction and sudden expansion [Fried and Idelchik, 1989].

Turbulence can be reduced by minimizing these transition spaces. One method is to incorporate media into the empty spaces. This method was used in the reduced volume filters that will be discussed later. Experiments have shown [Jaroszczyk, T. at al, 2004] that at a nominal engine flow rate, the pressure drop of a panel filter housing can exceed the pressure drop of a clean panel-type filter element by a factor of three.

Figure 1 shows flow pattern in the traditional panel air induction system and in a Direct Flow air cleaner. The pressure drop in a panel filter drastically increases in the transitions between the inlet and the housing and the housing and the outlet. The smooth transition in the Direct Flow and other in-line filters minimizes flow restriction.

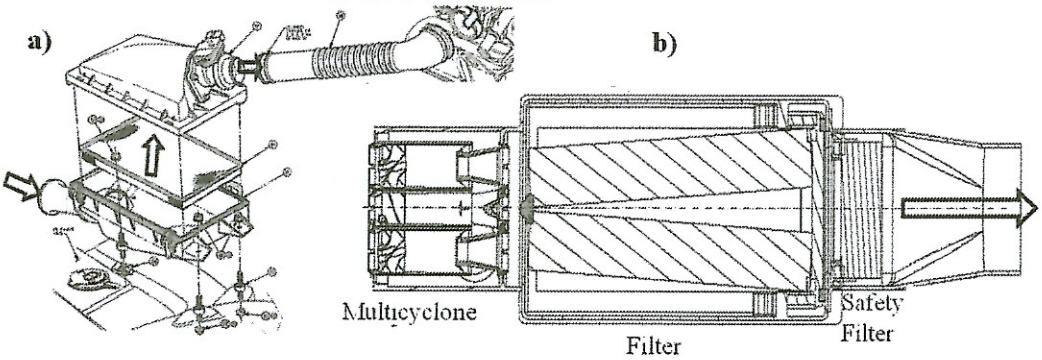

Figure 1. Schematic view of a Panel Filter- a) Direct Flow filter- b)

2. In-line (Axial Flow) or Reduced Volume Filters

A historical view of automotive air filters was probably first published by Clarke Rodman [Rodman, 1998]. The development of panel and cylindrical filter elements, and filter media is discussed. Here, we will focus on the recently introduced in-line or reduced volume filters constructed of flutes or pleated media blocks.

In-line or reduced volume filters, those having a high media utilization coefficient, are a relatively new family of engine air filters gradually reaching the engine air filtration market. These filters have been designed to meet the requirements for small packaging while at the same time maintaining or exceeding high performance. The axial flow pattern avoids turbulences by allowing the aerosol to flow straight through the filter. It leads to the decrease of potential pressure losses.

The Donaldson PowerCore filtration technology [Donaldson Brochure, 2002, DIESEL PROGRESS North American Edition, 2008, Donaldson Presentation, July 2009, Adamek, 2008] that combines axial-flow filer design with Ultra-Web® nanofiber filter media technology is the most known design. It has been employed mainly in the following applications: truck, construction equipment, agriculture, and power generation. On-highway applications still remain the major application of the PowerCore fluted filters with nanofiber filter media. More than 5 million filters have been sold. Donaldson PowerCore filter technology has 27 patented features.

The PicoFlex® filter utilizing triangle flutes [Mann+Hummel PicoFlex® Brochure, 2004, Peltz et al, 2003] is the second fluted design that has reached the engine air filter market. The CompacPlus® filter element (Figure 2d) has 50% more filter media surface area than the conventional filter element. Currently, Mann + Hummel offers the IQORON air cleaner series made of pleated media blocks (Figure 3). The air cleaned may be equipped with high efficiency multi-cyclone block precleaner that is a standard or optional separation stage used in many in-line air cleaners.

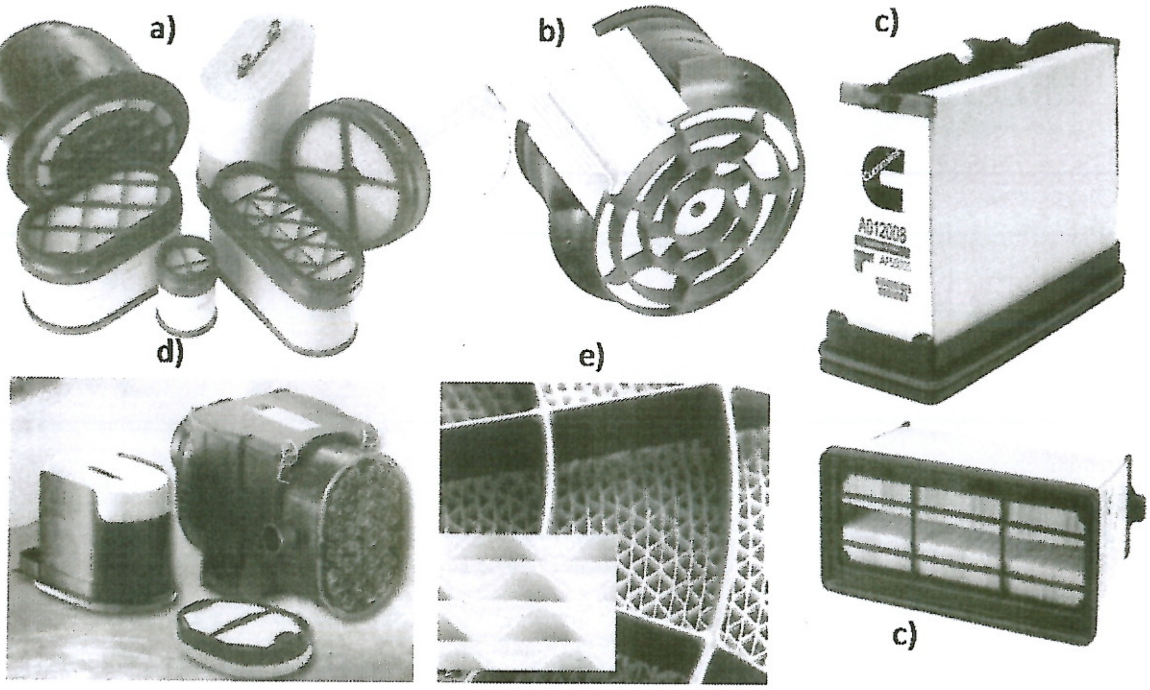

Figure 2. In-line fluted and pleated air filters: a)-Traditional PowerCore - (Donaldson), b) - Channel Flow (Baldwin), c) Direct Flow – Cummins, d) - PicoFlex - (Mann+Hummel, e) – block of flutes

The third successful fluted design was introduced by Baldwin [Baldwin brochure - form 346] as the Channel Flow® Air Filters. According to Baldwin, the design allows a reduction of the amount of space by up to 50% when compared to traditional filters. Examples of all known in-line fluted air filters are shown in Figure 2.

The fluted design shown in Figure 2 can have an oval or triangle shape. The design and flow pattern are discussed in details elsewhere [US Pat. Des. 396,098, US Pat. Des.

437,402]. The fluted design has been known for decades, [US Patent 2,210,397, 1940; US Patent 2,259,092,1952, US Patent 3,025,964, 1962; US Patent 4,430,223, 1984] to mention a few. These filters are discussed in detail by Pratt [Pratt, 1985]. However, Donaldson was the first company that successfully delivered this solution to the market reaching both the original equipment and aftermarket applications. The success was possible by combining the optimized design, advanced nanofiber media technology and efficient production technology. Determined support of these three areas led to the development of Donaldson PowerCore™ G2 filters with 30 percent smaller footprint with the same straight-through airflow and high-density filtration system as the "original" PowerCore and 50% size reduction when compared to the traditional cylindrical filters. This technology was introduced at the 2008 ConExpo-Con/Agg Show in Las Vegas in March. Examples of PowerCore™ G2 filters are shown in Figure 3. The filters can have cylindrical, oval, and rectangular shapes.

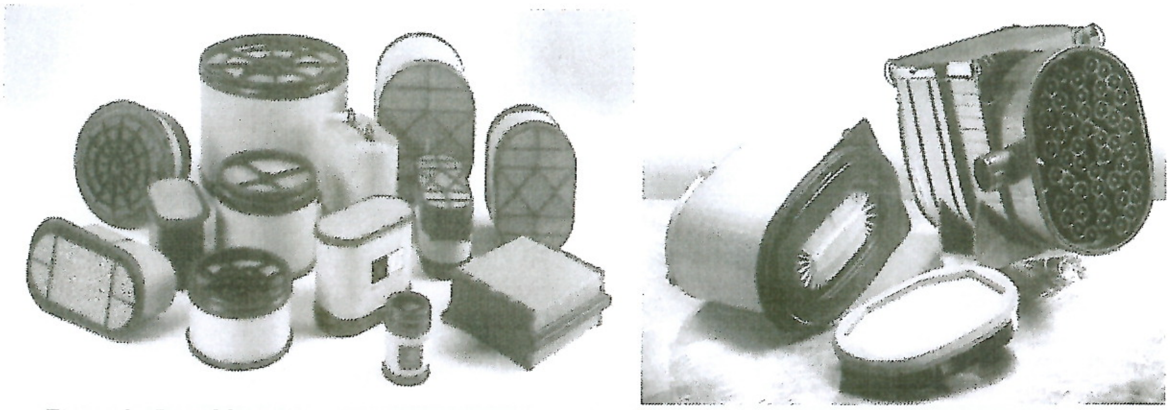

Figure 3. Donaldson PowerCore™ *G2 filters on the left and Mann+Hummel IQORON designs*

Although straight-though flow filters have been known for a long time [US Patent 4,157,902, 1979], the conical design [US Patent 5,106,397, 1991, US Patent Design 342,900, 1991] that was introduced by Ford in the 1990's was one of the first designs that reached the market. The filter fully utilizes the low resistance coefficient of the bullet shaped insert and the flow-straining feature of open pleats at the filter element inlet. The bulleted inlet is not used in the Mann + Hummel IQORON design with similar approach to the main filter design. For an almost identical media surface area, the pressure drop of the conical filter element is only 46% of the panel filter element. Pressure drop for the conical air cleaner, including housing and the filter element, is 39% lower than its panel filter counterpart [Jaroszczyk, et al, 2004].

In contrast to the fluted designs, the Cummins Direct Flow axial filters that were first patented in 2002, utilize alternating sealing technology [US Patent 6,375,700, U.S. Patent 6,482,247, U.S. Patent 6,511, 599, US Patent 7,314,558, US Patent 7,323,106, U.S. Patent 7,097,694]. The majority of the Direct Flow design incorporates equalized contaminant passages in the form of spaces between individual pleated elements, which prevents such clogging (Figure 2c). The pleating technology used in the construction of Direct Flow filters enables the use of high-speed rotary pleaters. Such elements can be added to obtain a larger filter as flow rate increases, filtration performance specifications change (increases in dust capacity or efficiency) or dust concentration increases. The individual pleated filter elements are sealed with a leak-free bond on one end and open on the opposite end. This type of design prevents contaminant from leaking without being filtered to the required level of particle size and concentration. Figure 4 shows Donaldson Power Core air induction system and Cummins Direct Flow air cleaners. The Figure shows that the dust cake is uniformly distributed on the entire length of the flute. This is a positive feature since uniform dust cake contributes to greater dust holding capacity of the filter.

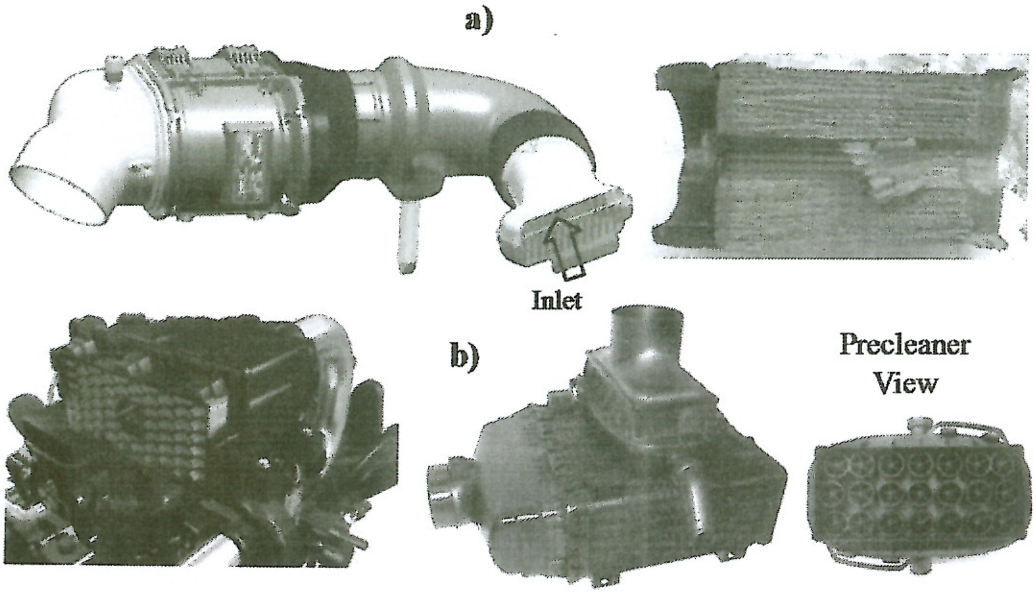

Figure 4. a) - Donaldson's Power Core air induction system on the left and dust cake in the filter, b) - Cummins Direct Flow air cleaners, left – on an engine, center – assembly

The frictional forces, flow around pleats or flute edges, and the flow across the filter media are the main factors responsible for flow restriction. The optimum flute length is typically between 150 - 300 mm. The length of the pleated in-line filters can be greater.

Because of the relatively small volume of the in-line air cleaners, they can be incorporated with a large engine (Figure 4) under the hood, or just behind the truck cabin.

3. The Role of Nanofibers in Engine Air Filtration

Dust cake filtration dominates in an engine's main filters, which are commonly made of cellulose or synthetic pleated thin filter media. When dust particles deposit inside the media, the porosity decreases and the effective fiber diameter increases. As a result, filter efficiency increases and pressure drop increases (for fine dusts, drastically) because decreased porosity causes increased air velocity inside the partially clogged media. At the same time, the efficiency decreases because of increased fiber diameter. To avoid drastic pressure drop increase, particles, especially the fine "clogging" type, should be kept on the media surface. This can be done by applying nanofiber to the media influent side. Moreover, when the particles accumulate as a dust cake on the nanofiber media surface, they can be easily removed by shaking, or reverse flow, or even filter vibration during motor vehicle operation. Pressure drop in cellulose media can be described by an equation [Myedvyedyev et al. 1984] $\Delta p = \dfrac{\mu \cdot v \cdot m \cdot h}{d_f^2 \cdot \rho_f(-0.984 \ln \beta - 0.47)}$, where μ = air dynamic viscosity, m = media basis weight, h = media thickness, ρ_f = fiber density, ß = filter solidity (or packing density) - volume of fibers/volume of filter. Pressure drop here is a function of $1/d_f^2$ (d_f = fiber diameter) and is a linear function of media thickness h and a complex function of packing density. Pressure drop in the free molecule and slip regions is a function of $1/d_f$ [Pich, 1969, 1971; Cheng et al, 1988] that occurs when fiber diameter is below approximately 400 nanometers under standard flow conditions. Therefore, nanofibers are essential to achieving a high efficiency of particle removal at relatively low-pressure drops as it described by an equation $\Delta p = 2.29\frac{\mu \cdot v \cdot m \cdot h}{r_f \cdot \lambda}$, where r_f is fiber radius [Pich, 1969].

Because of the dependency of the efficiency and pressure drop on fiber size and because of slip flow at the fiber surface, nanofibers become highly desirable for filtration applications [Kosmider and Scott, 2002]. In other words, when fiber diameter decreases to nanometers, the gas flow is in the molecular (or transition) regime and the pressure drop decreases. However, this is valid only for clean filters. When dust deposits are formed on nanofibers, this benefit of low-pressure drop reduces with increased amount of the dust deposit. On the other hand, the permeability of nanofiber filter media is approximately 2.5 greater than the typical media used for commercial HD media applications (trucks, construction equipment, etc.). In other words, the pressure drop increase starts from 2.5 times lower initial pressure drop than the standard media. Therefore, the clogging process is longer. This is important especially for ultrafine particles since dust cake of fine particles has low permeability.

When the particles are uniformly distributed due to a huge surface area of the nanofiber layer, this cake causes less flow restriction. The specific surface area in the case of nanofibers is approximately 250,000 times greater than cellulose media. In the case of the nanofiber media, particles are attached to nanofibers that cover the pores. Therefore, they cannot penetrate the filter. In contrast, the pores stay open in the cellulose media; thus, small particles can penetrate the media and reach the engine combustion chamber. Dust particle distribution on cellulose and nanofiber filter media is shown in Figure 5.

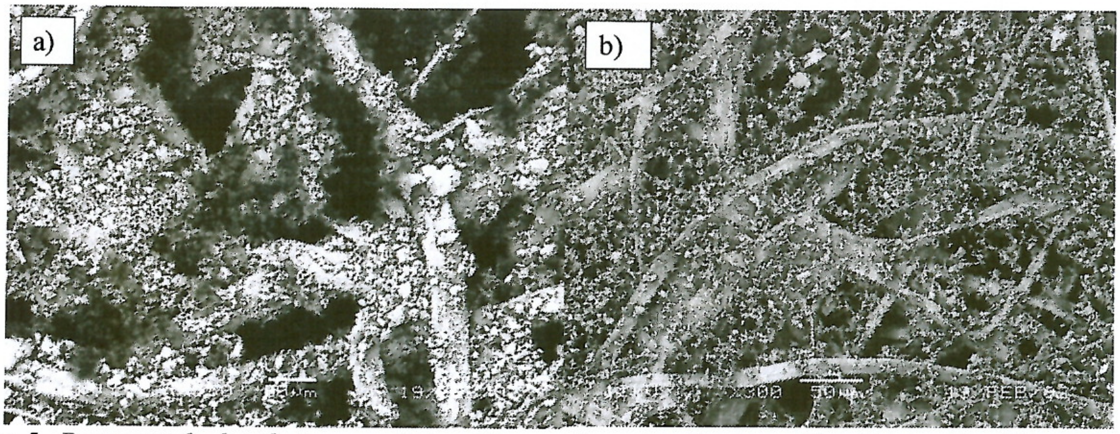

Figure 5. Dust particle distribution on cellulose filter media – a) and on nanofiber filter media – b)

Nanofiber filter media are not new in the filtration industry. In fact, the media reached specialized markets such as high efficiency filters for military ventilation, both mobile and stationary applications, and high efficiency face masks, more than 50 years ago [Filatov, 1997; Stokozov, 2002; Filatov, Budyka, and Kiriczenko, 2007]. The first factory that was using electrospinning was built in 1939 in the city of Tver to manufacture BF filters (military filters), [Filatov, 1997]. Mass production in other factories was initiated in 1964.

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The first patents on electrospinning were probably published in 1902 [J.F Cooley, US Pat. 692,631 and W.J. Morton, US Pat. 705,691]. Developments made by A. Formhals in 1934 [U.S. Patent 1,975,504] opened a door to commercialization. The cited work was performed on electrospinning from liquid solutions. Electrospinning from a melt was first patented by C.L Norton in 1936 [U.S. Patent 2,048,651]. However, Donaldson was the first company that successfully introduced nanofiber technology to industrial applications in 1981. In fact, research projects on this technology were initiated in early 1970s. The nanofiber filter media, known now under the name of Ultra-Web® media reached on-road and off-road diesel engine applications in 1993. The Endurance™ filters with extended service with the Ultra-Web media were introduced in 1993. In 1995, the self-cleaning Pulse Jet Air Cleaner (PJAC™) was developed in application to military high dust concentration environments. The proprietary electro-spinning process used to make the Ultra-Web® media became a great success. The Donaldson Ultra-Web nanofiber filter media technology is now protected by over 80 issued and pending patents. Mann+Hummel [Peltz et al, 2004, 2005] and Cummins [Jaroszczyk et al., 2008] consider nanofiber media in their reduced volume filters.

Nanofiber filter media are not an emerging technology any longer. Currently, nanofiber filter media are being offered in gas turbine air inlet, engine air, cabin, fuel, water, vacuum cleaning, and other markets. Moreover, production technologies, including the patented Nanospider™ electrospinning technology offered by Elmarco is available to media and filter manufacturers. The basic benefits of nanofiber media utilization are high efficiency filters, low pressure drop penalty, more compact, long life filters, "positive" dust shedding, and decreased re-entrainment of particles. There are still challenges, such as the increase in cost, chemical compatibility, durability – process and application, nanofiber layer adhesion and uniformity, and some hazards associated with solvent removal and disposal. As the use of nanofiber filter media expands, these manufacturing issues are being aggressively addressed.

Figure 6 and Table 7 show fractional efficiency as a function of particle size and pressure drop for various basis weights of nanofibers. It can be seen in the Figure that efficiency for the most penetrating particles increases from 10 to 43% when applying only 0.05 g/m^2 of nanofibers. The increase in pressure drop is approx. 27% for this basis weight of nanofibers. However, the substrate pressure drop is usually 3 to 6 times lower than the standard HD filter media in case of the cellulose substrate. The restriction of the final product is 2-4 times lower than for the commercial HD cellulose media.

Sometimes, the technology of electrospinning of nanofibers is compared with other technologies that provide much higher fiber mass output. The most important characteristic of this process is not the weight of nanofibers delivered by the process but the fiber size and fiber uniformity. Other processes can deliver a lot of fibers, but because of submicron and micron size of these fibers, at least 10 times more fibers are needed to obtain required filter performance. In the case of electrospun nanofibers only a very low basis weight, approximately 0.02-0.07 g/m^2 nanofibers with a diameter of 100 - 400 nanometers are applied to the cellulose or synthetic substrate to offer best in class filter media performance.

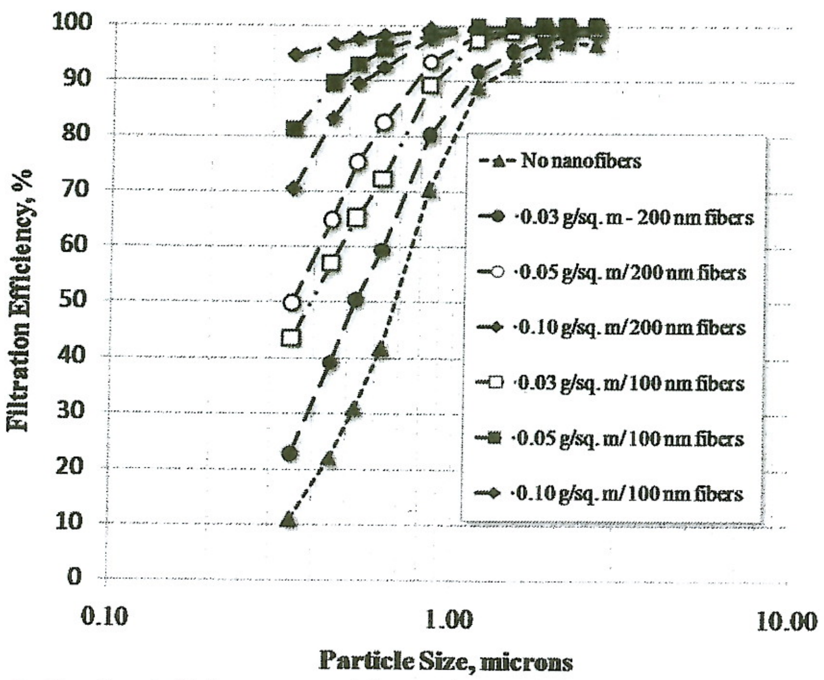

Figure 6. Fractional efficiency vs. particle size (microns) for various basis weight of nanofibers applied to a cellulose substrate

Table 7. Filter efficiency and pressure drop at media aerosol velocity of 16 cm/s = 2 50 cm/s at the filter face.

Substrate	**Nanofiber Basis Weight**	**Nanofiber Average Diameter**	**Filtration Efficiency**		**Pressure Drop**	
	g/m^2	nanometers	at 0.35 micron particle size , %	Efficiency Increase	mm of water	Pressure Drop Increase
Cellulose	No nanofibers	n/a	11	n/a	15.24	n/a
Cellulose	0.03	200	23	108%	17.53	15%
Cellulose	0.05	200	50	357%	19.3	27%
Cellulose	0.1	200	70	545%	24.13	58%
Cellulose	0.03	100	44	298%	18.8	23%
Cellulose	0.05	100	81	644%	22.61	48%
Cellulose	0.1	100	95	766%	29.21	92%

4. Conclusions:

- In-line fluted and pleated filters are offered in many different shapes that can be easily accommodated into reduced spaces of the current engine air induction systems.
- The smallest, high performance filters utilize nanofiber filter media.
- The nanofiber filter media, known now under the name of Ultra-Web® media reached the on-road and off-road diesel engine applications in 1993 and still dominate the engine nanofiber filter media.
- Nanospider^{TM} electrospinning technology offered by Elmarco is now available to media and filter manufacturers.
- Nanofibers offer high initial efficiency for small particles and fractional efficiency drastically increases when nanofibers are applied to a substrate. There is a direct correlation between filter performance and the amount of applied nanofibers.

- The new generation of the PowerCore systems called G2 can result in a 30% reduction in size from previous axial flow filters and a 60% reduction in size from cylindrical filters.
- By integration of the intake and exhaust systems in the new Cummins QSL9, the engine meets EU Stage IIIB and EPA Tier 4 Interim off-highway emission regulations. Moreover, the new system design results in efficient combustion that leads to reduction in fuel consumption by up to 5 percent, dependent on rating. Utilized here In-line Direct Flow filters are 35% smaller then the standard air cleaners.

ACKNOWLEDGMENTS

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3.3. Publikace 5:

Petrik, S. – Plistil, L.: **Olefinic Nanofibers for Filtration and Other Applications**. In: Proc. of SPE POLYOLEFINS/FlexPack 2011 CONFERENCE, February 27-March 2, 2011,Houston,TX.

Oponovaný článek ve sborníku mezinárodní konference organizované Society of Platics Engineers (SPE).

Přínos uchazeče:

Článek uvádí původní výsledky uchazeče a jím vedeného týmu na téma beztryskového elektrostatického zvlákňování tavenin polymerů (polyolefinů). Tento výzkum je motivován snahou vyloučit hořlavá a často zdravotně riziková rozpouštědla z procesu elektrostatického zvlákňování a současně vyvinout nanovlákenné materiály z chemicky odolných polymerů, jako je polypropylen, které se jinak velmi široce používají.
Uchazeč vedl výzkum v této oblasti, podílel se na vypracování metodiky a návrhu experimentů, včetně konstrukční koncepce prototypu laboratorního stroje, podílel se na zpracování a vyhodnocení výsledků. Napsal článek a přednesl přednášku.

OLEFINIC NANOFIBERS FOR FILTRATION AND OTHER APPLICATIONS

Stanislav Petrik and Lukas Plistil, ELMARCO s.r.o., Liberec, Czech Republic

Abstract

Electrospinning process from molten polymers has been investigated and discussed since several years, however, without any significant success in terms of process stability and fiber diameter distribution. The method is still very attractive because of its potential to enlarge "electrospinnable" family of materials (especially to polyolefins), and to solve environmental issues dealing with the use of solvents for processing of most polymers.

The paper will provide latest encouraging results obtained in Elmarco laboratories. Production process and nanofiber materials parameters will be introduced. The most important achievements are: low mean fiber diameter (down to 100 nm), improved fiber diameter distribution (close to the values typical for nanofibers electrospun from solvents), and scalability of the nozzle-less electrospinning equipment (Nanospider™). The challenging requirements for the polymers suitable for the process will be discussed.

Introduction

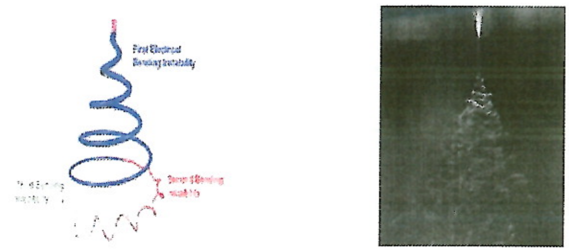
Electrospinning methods for creating nanofibers from polymer solutions have been known for decades [1, 2]. The nozzle-less (free liquid surface) technology opened new economically viable possibilities to produce nanofiber layers in a mass industrial scale, and was developed in the past decade [3]. Hundreds of laboratories are currently active in the research of electrospinning process, nanofiber materials, and their applications. Nanofiber nonwoven-structured layers are ideal for creating novel composite materials by combining them with usual nonwovens. The most developed application of this kind of materials is air filtration [4]. Liquid filters and separators are being developed intensively with very encouraging results. Also well known are several bio-medical applications utilizing nanofiber materials, often from biocompatible/degradable polymers like PLA, gelatine, collagen, chitosan. These developing applications include wound care, skin-, vessel-, bone-scaffolds, drug delivery systems and many others. [3, 5]. Inorganic/ceramic nanofibers attract growing interest as materials for energy generation and storage (solar and fuel cells, batteries), and catalytic materials [6-10].

To fully explore the extraordinary number of application opportunities of nanofibers, the availability of reliable industrial-level production technology is essential. This paper intends to demonstrate that the technology has matured to this stage.

Theoretical Background

The electrospinning process is an interesting and well-characterized physical phenomenon and has been an attractive subject for theoretical investigations of several groups [9, 11-17, 1, 2]. Most work concentrates on the essentials of the process – the nanofiber formation from a liquid polymer jet in a (longitudinal) electric field. It has been theoretically described and experimentally proven that the dominant mechanism is whipping elongation occurring due to bending instability [13, 16, 17]. Secondary splitting of the liquid polymer streams can occur also [1], but the final thinning process is elongation.

In Figure 1, the schematic of bending mechanism derived from physical model (a) is compared with a stroboscopic snapshot (b) [18].



a b

Figure 1. The path of an electrospinning jet (a – schematic, b – stroboscopic photograph).

(Courtesy of Darrell Reneker, University of Akron)

A comprehensive analysis (electrohydrodynamic model) of the fiber formation mechanisms published by Hohman et al. [16, 17] describes the regions of individual kinds of instability observed during the process. It has predicted and experimentally proven that there is a domain of the process variables where bending instability dominates.

The efforts to scale up the electrospinning technology to an industrial production level used to be based on multiplication of the jets using multi-nozzle constructions [1]. However, the number of jets needed to reach economically acceptable productivity is very high, typically thousands. This brings into play many challenging tasks, generally related to reliability, quality consistency, and machine maintenance (especially cleaning). The nozzle-less electrospinning solves most of these problems due to its mechanical simplicity, however, the process itself is more complex because of its spontaneous multi-jet nature. The Lukas' et al. [19] study focused on the process of multi-jet generation from a free liquid surface in an electric field. They showed that the process can be analyzed using Euler's equations for liquid surface waves, and derived the dispersion law for the waves in the form

$$\omega^2 = (\rho g + \gamma k^2 - \varepsilon E_0^2 k)\frac{k}{\rho} \quad (1)$$

where E_0 is electric field strength, γ – surface tension, and ρ is the liquid density.

When a critical electric field intensity is reached (E_c), ω^2 is turned to be negative, ω is then a purely imaginary value, and hence, the amplitude of the liquid surface wave exponentially grows, which leads to an instability.
Critical field strength can then be expressed

$$E_c = \sqrt[4]{4\gamma\rho g/\varepsilon^2} \quad (2)$$

From this equation, they derived the expression for the spatial period („wavelength") – the average distance between individual jets emerging from the liquid surface (Figure 2).

$$\lambda = 12\pi\gamma/[2\varepsilon E_0^2 + \sqrt{(2\varepsilon E_0^2)^2 - 12\gamma\rho g}] \quad (3)$$

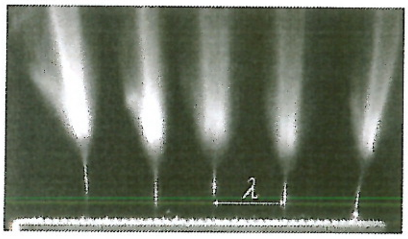
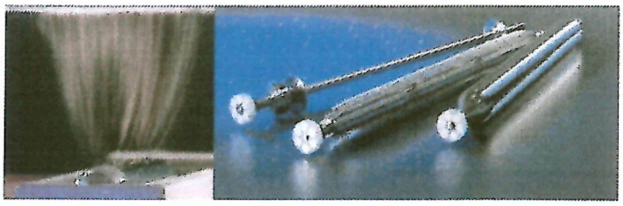


Figure 2. Free liquid surface electrospinning of Polyvinyalcohol at 32 kV. *(Courtesy of David Lukas, Technical University of Liberec)*

Technical Realization

The simplest realization of the nozzle-less electrospinning head is in Figure 3. A rotating drum is dipped into a bath of liquid polymer. The thin layer of polymer is carried on the drum surface and exposed to a high voltage electric field. If the voltage exceeds the critical value (4), a number of electrospinning jets are generated. The jets are distributed over the electrode surface with periodicity given by equation (6). This is one of the main advantages of nozzle-less electrospinning: the number and location of the jets is set up naturally in their optimal positions. In the case of multi-needle spinning heads, the jet distribution is made artificially. The mismatch between "natural" jet distribution and the real mechanical structure leads to instabilities in the process, and to the production of nanofiber layers which are not homogenous.

Several types of rotating electrodes for free liquid surface electrospinning for industrial machines have been developed (Figure 3b). However, the drum type is still one of the most productive.



a **b**

Figure 3. Free liquid surface electrospinning from a rotating electrode (a), and various types of spinning electrodes (b).

Research and development centers are very active in their efforts to further improve productivity of the manufacturing process. Novel methods for the production of sub-micron fibers are being developed. The most advanced methods alternative to electrospinning are "Fine Hole" meltblown and "Islets-in-the-sea". The individual methods can be considered to be complementary rather than competing. This is especially true with respect to the fiber diameter distribution and fiber layer uniformity. Individual methods will likely find different areas of application. More productive Nano-meltblown and Islets-in-the-sea technologies compromise fiber diameter and homogeneity and will likely be used in production cost sensitive applications like hygiene nonwovens, while high quality electrospinning technologies will be used in products where their high added value and need for low amounts of the material can be easily implemented (air and liquid filtration, biomedicine).

The nozzle-less principle using rotating electrodes has been developed into a commercially available industrial scale. A photograph of a modular Nanospider TM machine is in Figure 4.

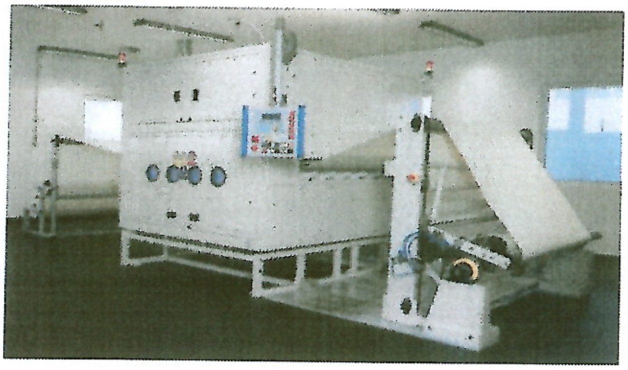


Figure 4. Nozzle-less production electrospinning line (Nanospider^{TM}).

Melt Electrospinning

Electrospinning of molten polymers is attractive from several reasons: It is a "green" technology (no solvents used), allowing to process hardly soluble polymers (PP, PE, PET, etc.), promissing certain increase of the process troughput. However, there are also several challenging task to be solved, related especially to the higher requirements on polymer quality (optimal melt viscosity, conductivity, or polarity).

Published results from the trials to electrospin polymers from melts were not competitive so far to the solvent-based approach. The best published data [20] showed relatively thick fibers: 270±10 nm obtained with a PEG-PCL copolymer, using a special needle setup, and 840±190nm obtained with a PP (MFI 15g/10min) – Irgatec blend. The development of melt electrospinning technology at Elmarco began in 2006. Initial experiments had been done with a Copoly(ester-amide) (PEA) polymer with the general structure:

—[—soft polyester segment—]$_y$— [—hard polyamide segment—]$_x$—

Main features of the material are:

- good rheological properties: zero shear viscosity 2.3 Pas at 190°C,
- mp 120-130°C, Tg -60°C, degradation starts at 220°C,
- high crystalization rate,
- melt viscosity can be controled by the ratio of soft and hard segment,
- hydrophilic, well soluble in chloroform and simple organic acids.

The fibers were made on a laboratory Nanospider^{TM} machine with heated wire rotating electrode and heated bath (Figure 5). The PEA crude polymer was spinnable, no blending or treating was needed.

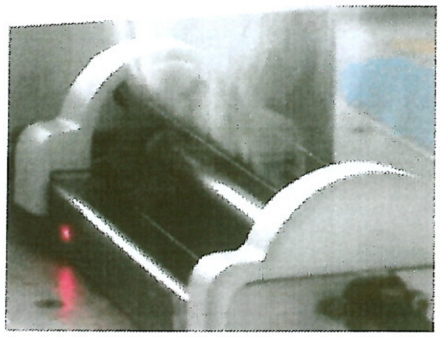


Figure 5. Nozzle-less melt electrospinning at 20 cm rotating electrode.

Filtration performance of the PEA nanofiber layer deposited at the cellulose substrate passing the machine at a constant speed of 1 m/min is illustrated in Figure 6.

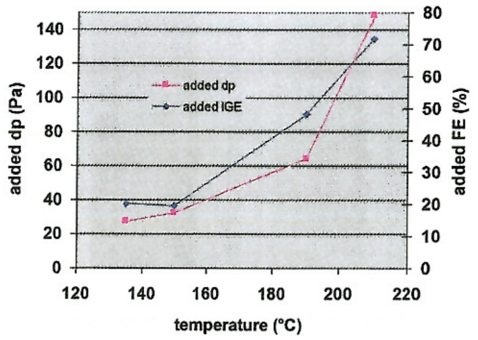


Figure 6. Increase of pressure drop and filtration efficiency as a function of PEA melt temperature.

The data in Figure 7 were obtained at 50 l/min air flow and samples area 100 cm^2 (corresponding to air speed 5 m/min). The filtration efficiency (FE) was measured using 0.3 μm NaCl particles. The result indicates the decrease of mean fiber diameter and increase of the process productivity caused by the change of the rheological properties of the melt.

Based on the experience gained from laboratory trials, a prototype 1.6 m wide production machine was built using the concept of the 2nd generation Nanospider machines [21]. A static heated wire has been used as spinning electrode. The polymer is deposited on the wire by a moving carriage, as schematically shown in Figure 7.

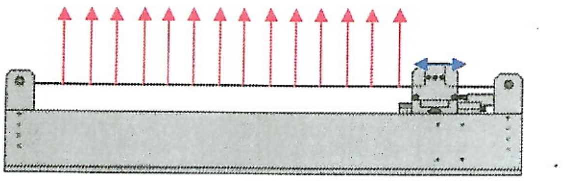
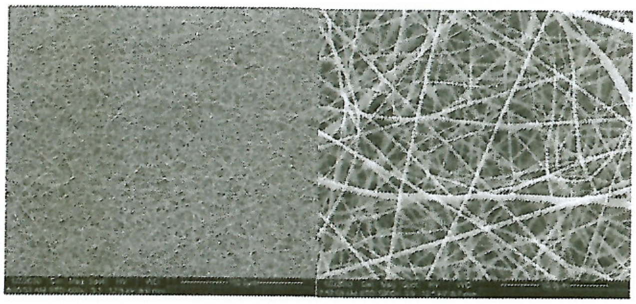


Figure 7. Schematic of the spinning electrode system of the production 1.6 m prototype line.

The production process on the 1.6 prototype machine has been tested with several polymers (PEA, Polypropylene, Polycaprolactone). In Figure 8, good homogeneity and fiber diameter distribution of a PEA nanofiber layer is demonstrated.



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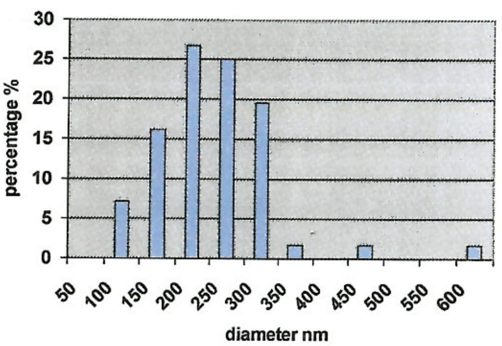

b

Figure 8. PEA nanofibers produced at 1.6 m prototype line: a – SEM picture, b – fiber diameter distribution.

The long-term process stability and homogeneity of the produced air filtration media is illustrated in Figure 9. Similar encouraging results were obtained with Polypropylene and Polycaprolactone, however, these polymers needed additive treatment to adjust melt rheological and electrical parameters to acceptable values.

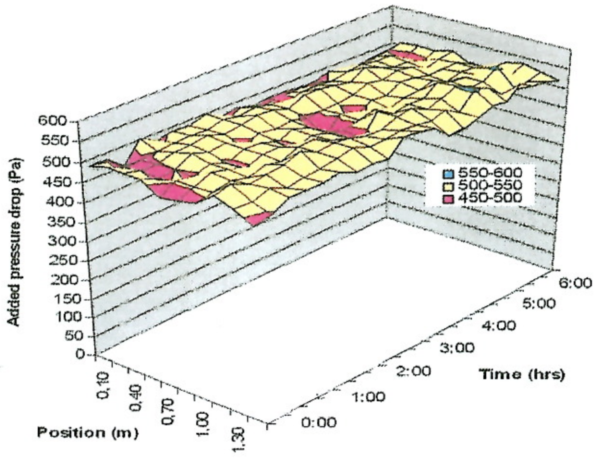

Figure 9. Homogenity of PEA melt e-spun NF layer in time and width (200 °C, 120 kV, fabric speed 0,3 m/min, air flow: 50 l/min, 100 cm^2, 5m/min).

Conclusion

High-quality low-cost production of nanofiber layers is essential to support the enormous amount of research results being obtained at many universities and research centers. The described nozzle-less electrospinning technology has matured to a level where large scale production use is common, and can be modified for practically all known polymers soluble in organic solvents and water, as well as for polymer melts. This opens commercial opportunities for hundreds of ideas developed in the academic sphere.

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Key Words: nanofibers, electrospinning, melt, polyolefins, filtration, nanospider, nozzle-less.

4. Další aplikace nanovlákenných materiálů

Významný podíl na výzkumných aktivitách uchazeče je v oblasti vývoje dalších aplikací nanovlákenných materiálů, které mají vysoký komerční potenciál a jsou proto předmětem intenzivní snahy dovést příslušnou technologii do průmyslového měřítka. Uchazeč vedl výzkum v této oblasti, podílel se na vypracování metodiky a návrhu experimentů. Přiložená práce (*Publikace 6*) ilustruje výsledky uchazeče a jeho týmu v několika oblastech:

a) Filtrace
V práci jsou ilustrovány přínosy nanovlákenných materiálů při konstrukci filtračních médií. Uvedeny jsou výsledky měření filtrační účinnosti a tlakového spádu těchto materiálů v závislosti na množství a průměru nanesených nanovláken ve srovnání s konvenčními médii bez nanovláken.

b) Zvuková absorpce
Nanovlákená membrána vložená do klasického mykaného vlákenného substrátu v „sendvičovém" uspořádání přináší výrazné zvýšení zvukoabsorpčních vlastností především v oblasti nízkých frekvencí, což je velmi zajímavé například pro použití v automobilovém průmyslu, v domácích spotřebičích (pračky, myčky) nebo ve stavebnictví. Masovému rozšíření těchto materiálů zatím brání vyšší výrobní náklady.

c) Fotokatalýza
Použití polymerních nanovláken v kombinaci s nanočásticemi a nanovlákny z oxidu titaničitého se ukázalo jako výhodné pro vývoj fotokatalytických filtrů. Nanovlákenná vrstva brání uvolňování nanočástic do okolního prostředí, přitom je vysoce permeabilní pro filtrované médium (vzduch). V práci jsou uvedeny experimentální výsledky ověření prototypu fotokatalytického vzduchového filtru.

d) Solární články
Elektrolytické solární články za bázi elektrod z oxidů titanu mají potenciál především pro práci za nízkého slunečního svitu (při zatažené obloze). Motivací pro výzkum a vývoj uvedený v práci bylo využití anorganických nanovláken jako „nanodrátků" zlepšujících přenos elektrického náboje v materiálu elektrod, což vede ke zlepšení účinnosti článků. v práci jsou uvedeny výsledky výzkumu a vývoje nanovlákenných materiálů pro tuto aplikaci.

e) Baterie
Motivace pro výzkum v této oblasti je podobná jako u solárních článků: zlepšení přenosu náboje v elektrodách při zachování vysokého měrného povrchu materiálu (podstatné pro zachování kapacity baterií). V práci jsou uvedeny výsledky výzkumu nanovláken pro tuto aplikaci, včetně experimentálního ověření jejich funkčnosti.

4.1. Publikace 6:

Petrik,S. – Maly,M. – Rubacek,L. – Macak,J. – Stranska,D. – Duchoslav,J. – Coppe,A.: **Electrospun Nanofiber – The Tiny Layers that Add Great Value to Nonwovens**. In: Proceedings of the International Nonwoven Symposium 2009, EDANA, Stockholm, May 5-6, 2009 (ISBN: 2930159669).

Oponovaný článek ve sborníku symposia International Nonwoven Symposium 2009, EDANA, Stockholm, May 5-6, 2009.

Uchazeč přednesl vyžádanou přednášku na toto téma.

Přínos uchazeče:

Článek uvádí původní výsledky uchazeče a jím vedeného týmu z oblasti aplikací nanovlákenných materiálů pro filtraci, zvukovou absorpci, fotokatalýzu, elektrody solárních článků a baterií.
Uchazeč vedl výzkum v uvedených oblastech, vypracoval metodiku a návrh experimentů, podílel se na zpracování a vyhodnocení výsledků. Napsal článek a přednesl vyžádanou přednášku.

Electrospun Nanofiber
The Tiny Layers that Add Great Value to Nonwovens

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ABSTRACT

The principle, main features, and technical capabilities of the nozzle-less electrospinning technology (Nanospider™) will be presented in the paper. Nanospider™ position among other nanofiber nonwoven technologies is discussed.
Materials for final products used in several applications (filtration, sound absorption), and their recent test results are described and discussed. Newest achievements of the technology are presented: nanofibers from various polymers and inorganic materials. Wide range of applications of these unique new materials, e.g. devices for energy generation and storage – batteries, supercapacitors, fuel cells, solar cells, catalysts, and composite materials, are discussed.

1. Introduction

Electrospinning method for obtaining nanofibers from polymer solutions has been known since decades, but just 4 years ago, the revolutionary nozzle-less (free liquid surface) technology open full possibility to produce nanofiber layers in mass industrial scale. Nanofiber nonwoven-structured layers are ideal for creating novel composite materials by combining them with usual nonwovens.

The principle of the nozzle-less electrospinning technology is illustrated in the following graphics.

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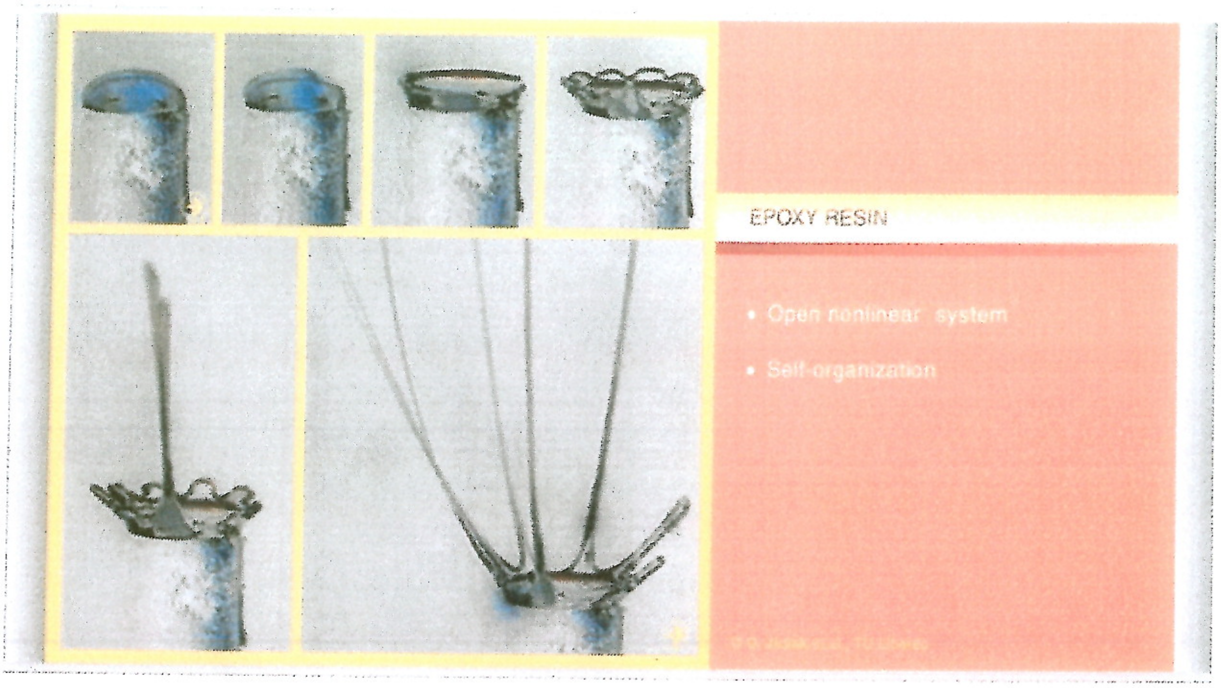

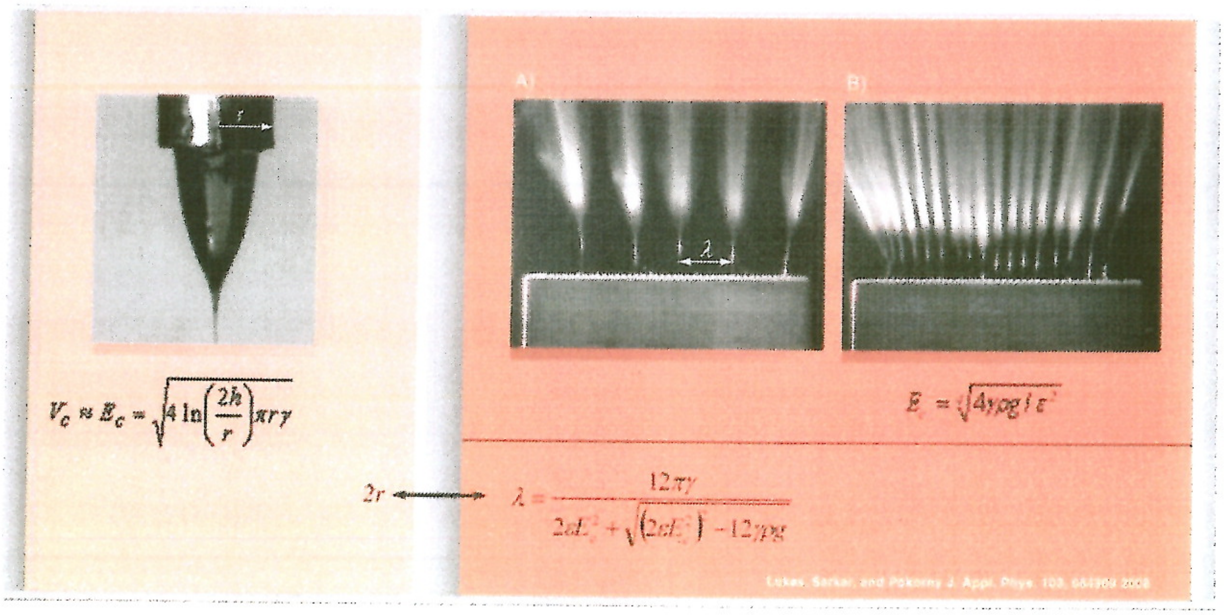

Fig. 1. Principle of Nozzle-Less Electrospinning

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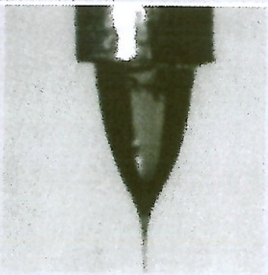
Tab.1. Comparison of Nozzle vs. Nozzle-Less Electrospinning

Production variable	**Needle**	**Nanospider™**
Mechanism	Needle forces polymer downwards. Drips and issues deposited in web.	Polymer is held in bath, even distribution is maintained on electrode via rotation.
Hydrostatic pressure	Production variable – required to be kept level across all needles in process.	None.
Voltage	5 – 20 kV	30 – 120 kV
Taylor cone separation	Defined mechanically by needle distances.	Nature self-optimizes distance between Taylor cones.
Polymer construction	Often 10% of solution.	Often 20% or more of solution.
Fiber formation path	Tortuous, subject to whipping.	Straight.
Fiber diameters	80, 100, 150, 200, 250 and higher. Standard deviation likely to vary over fiber length.	80, 100, 150, 200, 250 and higher. Standard deviation of +/- 30%.
		

Tab.2. Nanofiber Production Methods

	Extrusion		Electrospin	
Sub-type	Fine hole	Islets-in-the-sea	Needle	Nanospider™
Description	Fine fiber meltblown process, melted polymer is forced through small holes	Polymer blends are extruded through thicker holes, then separated afterwords, often hydro-entangled	Solvent polymers are forced through a needle and formed through an electrostatic field	Electrostatic field is used to form fibers but is formed without needles using higher voltage on roller-electrodes
Voltage	na	na	5 – 20 kV	30 – 120 kV
Fiber size (nm)	800 – 2,500 s = +/- 200%	800 – 2,500 s = +/- 200%	?? – 500 s = Varies	80 – 500 s = +/- 30%
Hydrostatic pressure	Yes	Yes	Yes	No
Production ready?	Yes	Yes	No	Yes

2. NANOFIBER APPLICATIONS: AIR FILTRATION

Nanofiber polymer layer deposited on regular nonwoven filter media usually shifts resulting air filtration parameters of this material several classes higher. A very fine nanofiber web of basis weight of 0.01 gm^{-2} to 0.1 gm^{-2} improves the filtration efficiency for submicron particles by hundreds of percent, while lowering the air permeability by only tens of percent. This evident benefit becomes to be widely commercially accessible due to the availability of productive industrial-scale Nanospider™ technology [1].

Usual parameter discussed (and required) by nanofiber filtration media users is the basis weight of nanofiber layer. However, experience with final (product) parameters of resulting filters shows, that there is not very strong correlation between basis weight, filtration efficiency and permeability (or pressure drop), at least in the case of cellulose substrate combined with relatively low-weight polymer nanofiber layer.

Mechanism of filtration process on fibrous media has been discussed in several publications [2-6]. For example, for cellulose filtration media of solidity β in the range of 0.11-0.33 and an average

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pore diameter of 12-84 μm, it has been shown that pressure drop depends on fiber diameter d_f according to relation [2]:

$$\Delta p = \frac{\mu \cdot v \cdot w_b \cdot h}{d_f^2 \cdot \rho_f \cdot (-0{,}984 \cdot \ln \beta - 0{,}47)} \qquad (1)$$

where μ is air dynamic viscosity, w_b - media basis weight, h - media thickness, ϱ_f - fiber density, β - filter solidity (or packing density) - volume of fibers/volume of filter.

However, in the case of low basis weight nanofiber layer, where molecular (or transition) flow regime takes place, following equation is considered to be valid [5]:

$$\Delta p = \frac{\mu \cdot v \cdot w_b \cdot h}{r_f \cdot \lambda} \qquad (2)$$

where r_f is radius of nanofiber and λ is mean free path of molecules.

Hence, the combination of cellulose medium with polymer nanofiber layer will require more complex models to describe behavior of final filtration material. Systematic experimental study of correlations between final product parameters (filtration efficiency, pressure drop) and morphology of cellulose/nanofiber media can provide useful data for both theoretical understanding of filtration mechanisms and practical design of air filters.

EXPERIMENTAL

Samples of controlled basis weight and fiber diameters were prepared. Nanospider™ production machine has been used, as it provides good long-term consistency of filtration media parameters (16 hours run with repeatability in the range of ±5%).

To obtain various basis weights, substrate speed had been varied from 0.2 m/min to 4 m/min for each series of samples, while polymer solution parameters (concentration, etc.) together with electric field intensity determined the range of nanofiber diameter. Nanofiber diameter distribution has been measured using scanning electron microscope (SEM). Basis weights were obtained either directly using analytical scale Mettler (higher values), or by extrapolation from its known dependence on substrate velocity (lower ones).
Pressure drop and initial gravimetric filtration efficiency have been chosen as representatives of product parameters. They were measured according to using NaCl aerosol at following settings: air flow speed: 5 m/min, sample area 100 cm^2, flow rate 50 l/min.

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RESULTS AND DISCUSSION

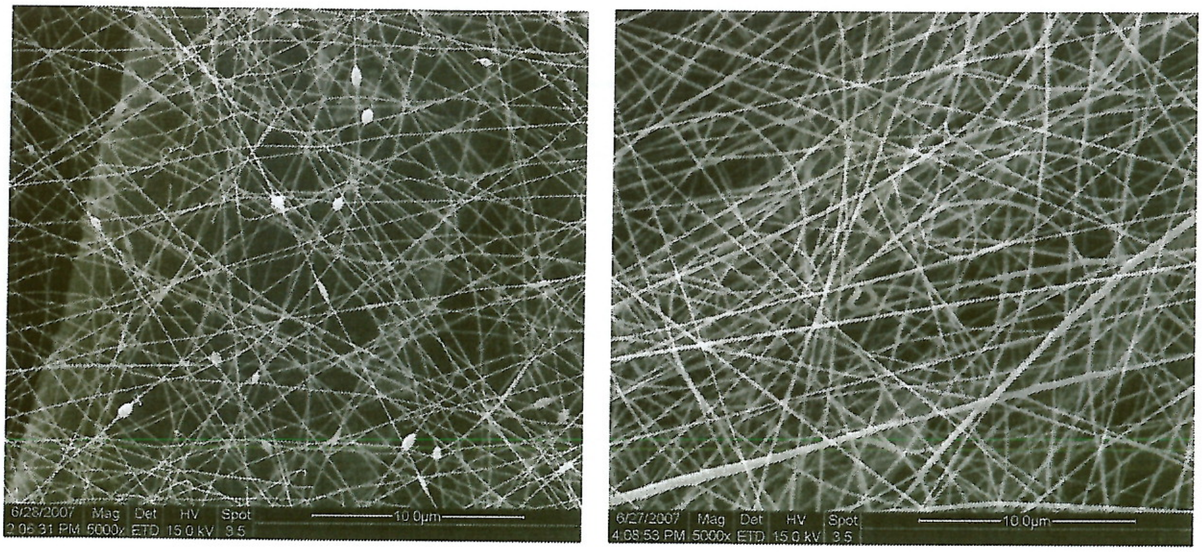
Samples in Fig. 2 show how different nanofiber layers can exhibit similar filtration properties. The first sample is made of thin nanofibers (around 80 nm) and lower basis weight (0.03 gm^{-2}), while the second one is characterized by almost 2-times thicker fibers (144 nm) and more than 3-times higher basis weight (0.10 gm^{-2}).

To consider the influence of both basis weight and fiber diameter on final product filtration parameters, we can define a simple value (Relative Fiber Length L_f) expressing the total length of nanofibers (in kilometers) deposited on unit surface of filtration medium (in square meters):

$$L_f = \frac{w_b}{\pi \cdot \rho \cdot \left(\frac{d_f}{2}\right)^2} \qquad (3)$$

where ρ is density of material of nanofibers.

As can be seen from the graphs in Fig. 3, both filtration efficiency and pressure drop are in much better correlation with Relative Fiber Length L_f than with nanofiber layer basis weight (w_b).



IGE = 73 ± 1 %
Δp = 168 ± 5 Pa

L_f = 6114 km.m^{-2}
w_b = 0.03 gm^{-2}
d_f = 83 ± 22 nm

IGE = 68 ± 1 %
Δp = 163 ± 4 Pa

L_f = 6128 km.m^{-2}
w_b = 0.10 gm^{-2}
d_f = 144 ± 36 nm

Fig. 2. Different nanofiber media with similar filtration properties

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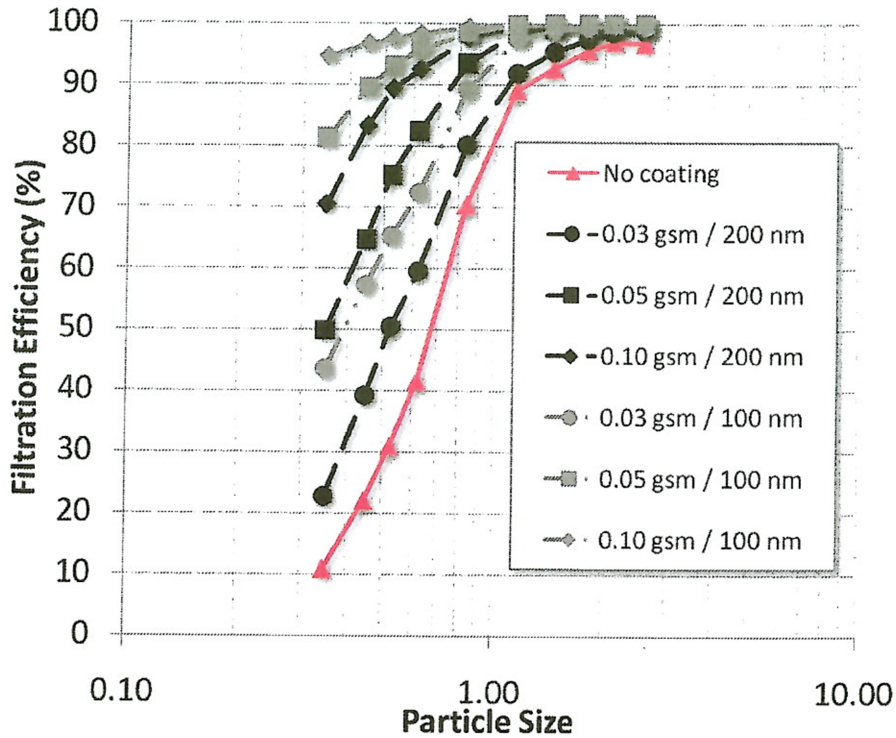


Fig. 3. Filtration efficiency of nanofiber media samples

Tab.2. Properties of nanofiber filtration media samples

Pressure drop for various coatings at 32 ft / min face velocity (equivalent to 490 ft / min based on pleated filter)						
Substrate	**GSM**	**NF Diameter**	**Filtration Efficiency**		**Pressure**	
		(nm)	**at 0.35 micron particle size (%)**	**D vs uncoated substrate**	**mm of H20**	**D vs uncoated substrate**
Cellulose	**No coating**	**n/a**	**11**	**n/a**	**15.24**	**n/a**
Cellulose	**0.03**	**200**	**23**	**108%**	**17.53**	**15%**
Cellulose	**0.05**	**200**	**50**	**357%**	**19.30**	**27%**
Cellulose	**0.10**	**200**	**70**	**545%**	**24.13**	**58%**
Cellulose	**0.03**	**100**	**44**	**298%**	**18.80**	**23%**
Cellulose	**0.05**	**100**	**81**	**644%**	**22.61**	**48%**
Cellulose	**0.10**	**100**	**95**	**766%**	**29.21**	**92%**

Experimental results obtained in this study showed that:

- Basis weight of nanofiber layer does not predict filtration parameters well enough. The same initial gravimetric efficiency can be obtained using nanofibers of very different mean diameters, or in other words, of very different basis weights.
- Filtration properties of cellulose media with low-weight polymer nanofibrous layer depend mostly on the total length of nanofibers per media surface unit ("Relative Fiber Length").
- "Relative Fiber Length" is in good correlation with both pressure drop and filtration efficiency.
- Image analysis of SEM pictures can be used for predicting of filtration properties of the media.

For more detailed understanding and predicting of filtration properties of the media studied here, it will be useful to investigate similar relationships using:

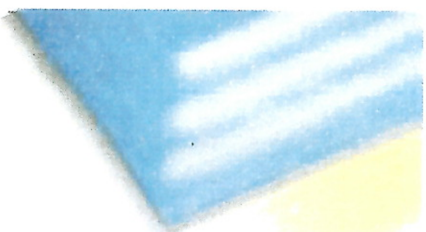
- Observations of the role of dust cake formed on media surface during filter lifetime or in field tests.
- Investigations of the effect of final filter design, pleating of the media, etc.

3. Nanofiber Applications: Noise Absorption

AcousticWeb™ is a new patented material with unique sound absorption properties. It is able to absorb sounds across a wide range of frequencies, especially standing out in the absorption of low frequency sounds below 1000Hz.

PRINCIPLE

Nanofibrous layer represents a membrane that vibrates at low frequencies. This characteristic is given by nanodimensions of the interfiber areas. Sound waves landing on the acoustic resonating membrane make the membrane oscillate and its amplitude is in its maximum in the case of resonance. Fiberous underlay material ensures the sufficient suppressing of the resonant membrane so that most of the sound energy accumulated in the resonator is transferred into the heat energy. Individual resonant elements are acumulated into one resonant system by lying these elements on each other.



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Structure of the material: Nanofibers layer are electrostatically spun on a carded web.

Nanofiber layer:
Material : Polyvinyl alcohol PVA
Mean nanofiber diameter: 350nm
Area weights : 0,2-0,8 gsm

Carded Web layer:
PES staple fibers with flame retarding modification, recycled cotton, etc.
Fiber fineness: 3,3-6,7 dtex

Advantages of Nanospider AcousticWeb™

- Excellent acoustic properties
- Very light-weight material
- Wide range of application
- Easy manipulation and processing
- Clean and safe operation
- Very good insulation properties
- (λ= 0,039 Wm/K)

Production line consists of the following components:

Carding machine – double doffer with 1,6 effective production width
Nanospider machine – 4 units with 8 spinning chamber
Lapper – transforms nanocoated carded web into to layerd material
Thermobonding oven – stabilizes the structure of the material
Cutting machine – formats material into the sheets

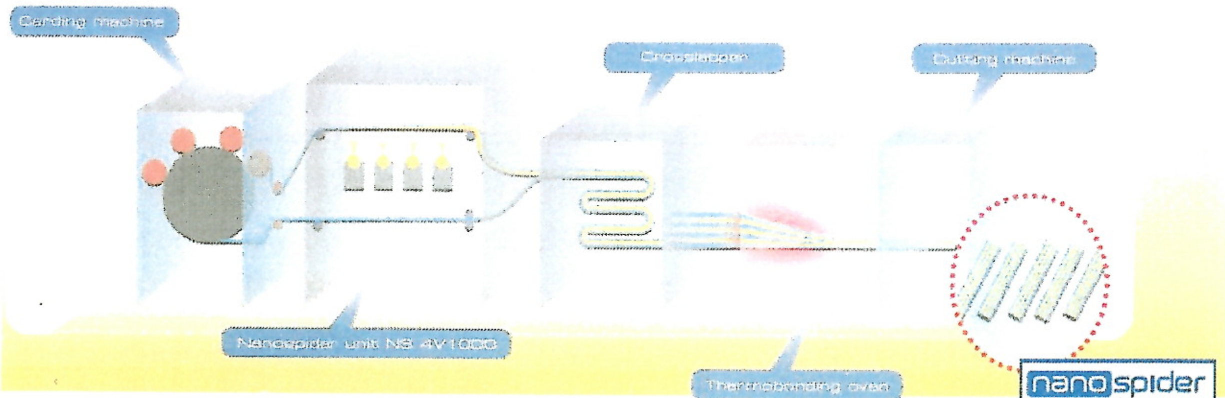

Fig. 4. Scheme of AcousticWeb production line

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Technical data:

- Production capacity – depends on final usage
    - 2 500 000 m^2 for 12 layered material
- Working width – 1,6m

4. Nanofiber Applications: Photocatalysis

PRINCIPLES OF PHOTOCATALYSIS

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl radicals: OH) able to undergo secondary reactions.

When the photocatalytic surface of a semiconductor catalyst (such as titanium dioxide-TiO2) is illuminated with energy equal to or larger than the bandgap energy (CB-VB), it excites the electrons from the valance band (VB) to the conduction band (CB), resulting in the formation of a positive hole (h+) in the valance band and an electron (e-) in the conduction band. The positive hole oxidizes either pollutants directly or water to produce •OH radicals, whereas the electron reduces the oxygen adsorbed to a photocatalyst.

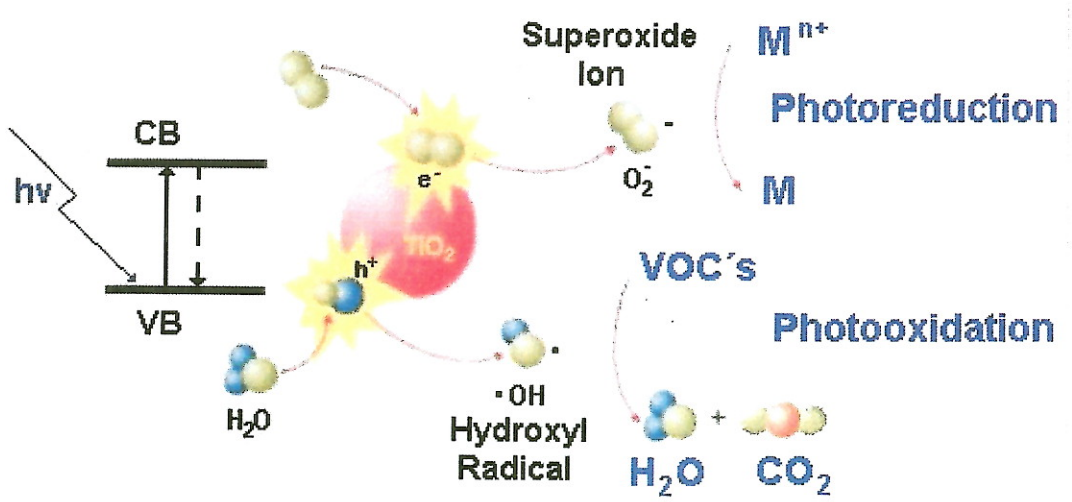

Fig. 4. Mechanism of photocatalysis

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Photocatalytic membrane features and usage

- Highly-permeable multi-layer composite based on polymer nanofiber structure as a supporting material for nano-structured catalyst.
- Nanofiber layers produced by Nanospider™ technology, enabling mass scale production.
- Nanofiber layers keep the catalyst inside and prevent its outlet, which can guarantee its safety.
- High efficiency of photocatalytic decomposition of Volatile Organic Compounds (VOC's) in air when compared to non-permeable PCA solutions.
- Designed for usage in photocatalytic air treatment in air purification systems, from stand-alone HVAC's to large buildings and industrial systems

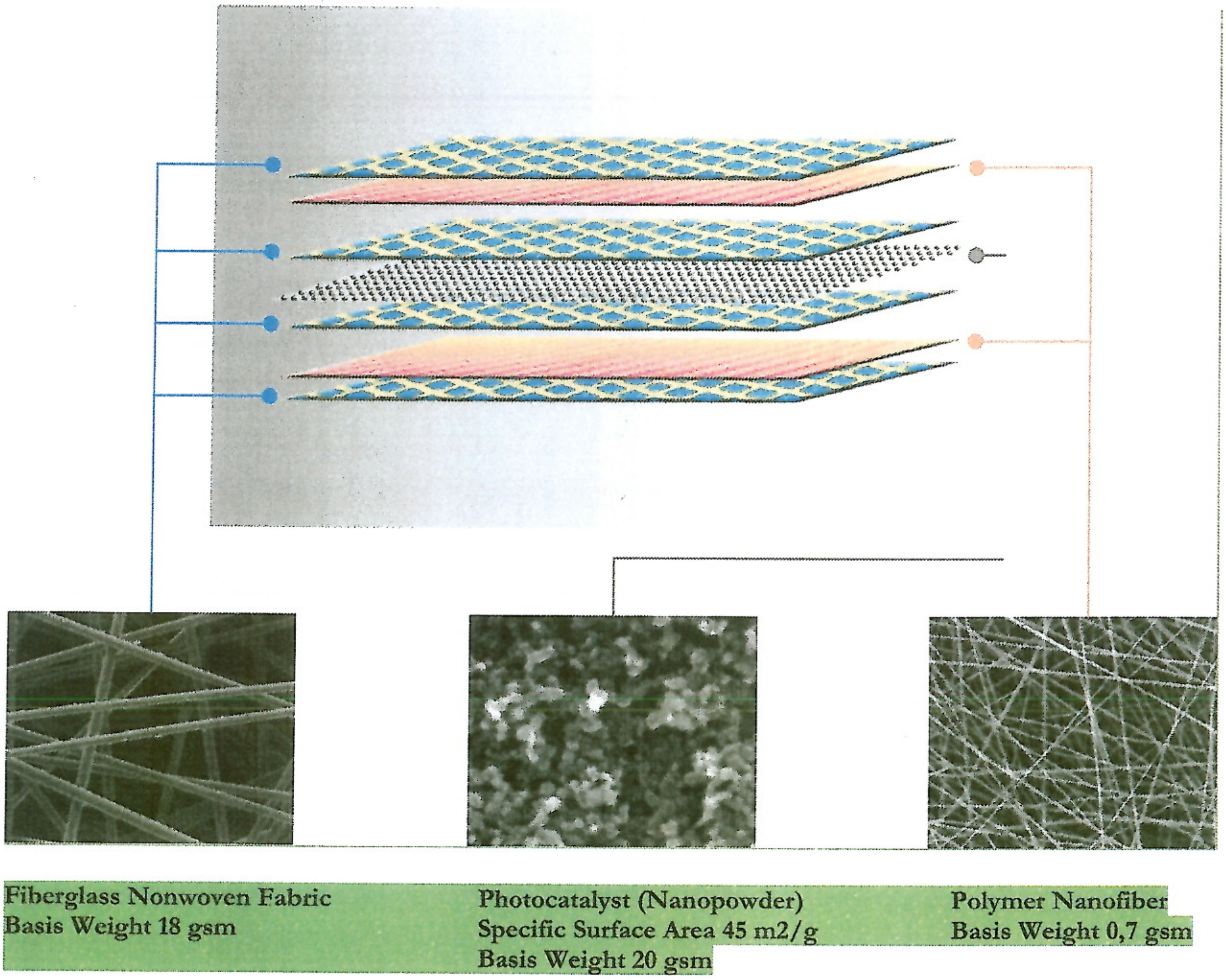

Fig. 5. Membrane composition

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Membrane properties

- Basis weight 112 g/m2
- Thickness 0,6 mm
- Pressure drop 155 Pa @ 50cm2, 48 l/min
- Filtration efficiency 75% @ 50 cm2, 48 l/min, particle size 0,3 μm

EXPERIMENTAL SETUP AND RESULTS

Ambient air with a relative humidity of 50-70% is mixed with an air stream containing VOC content at a ppm level. The obtained mixture goes through the photoreactor, where the air is purified (lowering of the VOC concentration) by the photocatalytic membrane. The pressure drop of the photocatalytic membrane is continually measured in the photoreactor. The concentration of VOC is displayed on a VOC monitor and the air flow mass is controlled by a flowmeter.

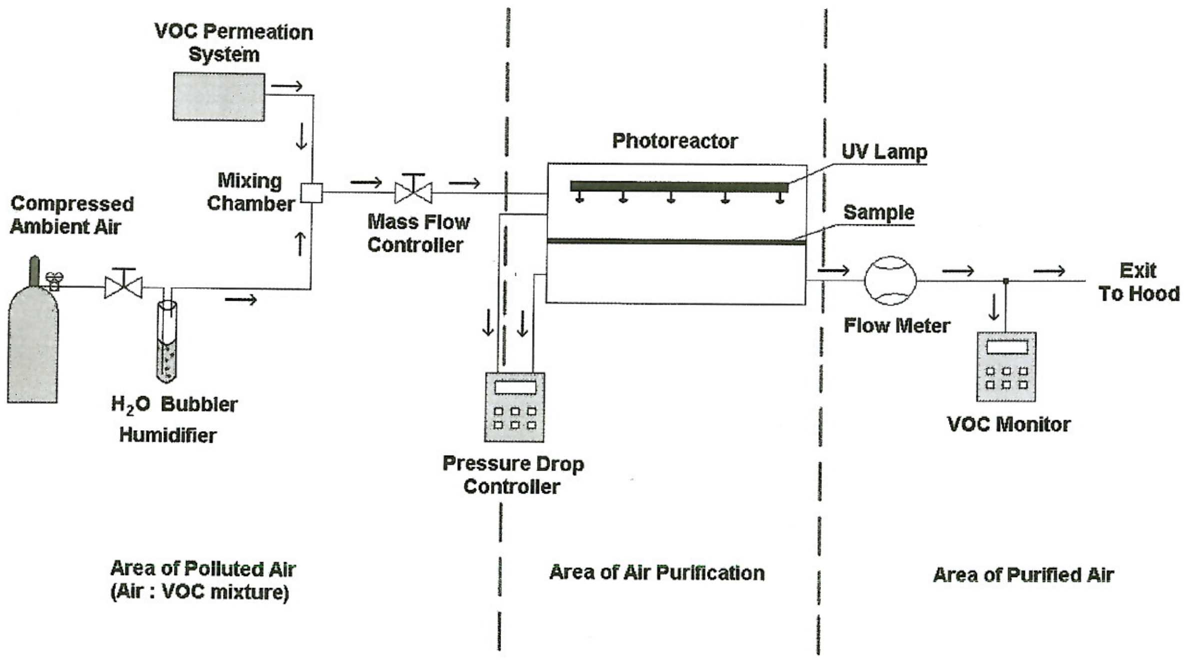

Fig. 6. Demonstration Apparatus: The Flow Scheme

Polluted air (air + VOC) flows across the photocatalytic membrane. While the UV lamp is off, the photocatalytic purification is inactive and the input VOC concentration "C1" is displayed. Turning the UV lamp on, the photocatalytic membrane starts the purification process and the concentration of VOC drops to the lower level "C2".

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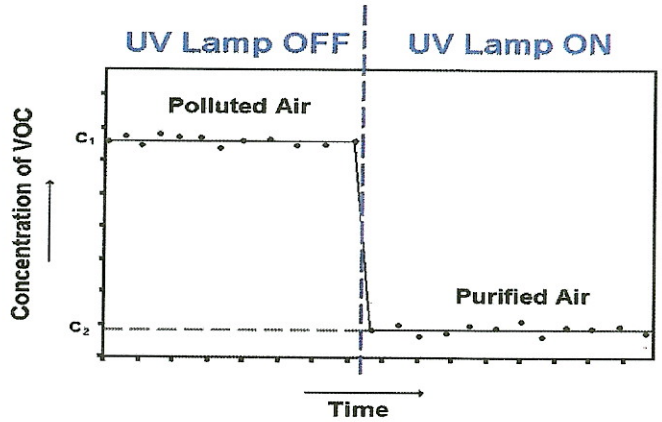

VOC's Conversion Efficiency $= \frac{C_{1\,(polluted\ air)} - C_{2\,(purified\ air)}}{C_{1\,(polluted\ air)}}$

Fig. 7. Photocatalytic behavior of the membrane

5. Nanofiber Applications: Solar Cells

Nanofibers unique architecture provides an almost linear path as the electron carrier. Losses in the material while travelling are significantly lowered, resulting in higher conversion efficiency. Additionally, nanofibers can harvest more photons (thus making more electrons) because they are more accessible for the light when compared to nanoparticles.

Nanofibers embedded in the DSSC module can make up to 25% more energy than conventional DSSC modules with nanoparticles.

PHOTOVOLTAIC TECHNOLOGIES

Photovoltaic modules convert the light energy from the sun into electricity. The photovoltaic effect occurs when photons from sunlight are absorbed by a photovoltaic solar panel, knocking electrons into a higher state of energy, creating electricity. There are several photovoltaic technologies currently in use today:
- Silicon-based solar cells
- Thin film solar cells (CdTe, CIGS etc.)
- Dye-sensitized solar cells (TiO2/dye) – Nanofibers can significantly enhance this material
- Single or multi-junction concentrators (GaInAs, GaInP, etc.)
- Organic-based solar cells

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The principles of DSSC operation are shown on the graphic. To make a DSSC, TiO2 (nanoparticles or nanofibers) are coated with a ruthenium-based dye that absorbs a wide range of wavelengths given off by sunlight, and is then placed between two electrodes (conductive glass). An electrolyte solution containing iodine ions fills the volume in between. Upon illumination, the dye absorbs photons and injects electrons into a 5-10 μm thick layer of TiO2 that efficiently transports electrons through the conducting glass electrode into the circuit making electricity. The excited state of the dye is regenerated by the iodine ions that take electrons from the other electrode (typically coated with platinum).

DEMONSTRATION APPARATUS

Two different photovoltaic cells are compared:
- The commercially available silicon-based solar module
- Four DSSC in a series

Both modules are illuminated by the same light source and the level of illumination is reduced step-by-step. The DSSC exhibits a more stable power output when compared to the silicon-based cell under low illumination. An ammeter is connected to each module. At certain (very low) levels of illumination, the DSSC gives even higher output than a silicon-based cell.

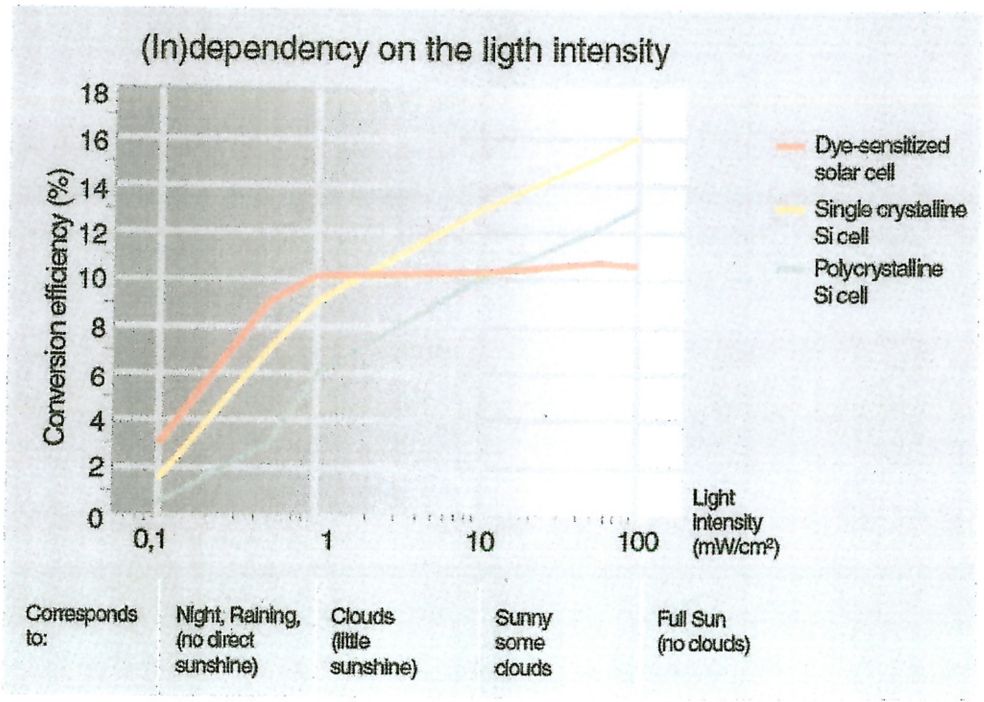

Fig. 8. Characteristics of DSSC

ADVANTAGES OF DSSC OVER OTHER TECHNOLOGIES

- Less dependent on the light source – can harvest light energy coming from direct sunlight and artificial light sources
- Performance is much less sensitive to the intensity of the light source
- Can be made transparent – opens exciting possibilities to be placed on windows of buildings
- Flexibility – allows integration into mobile devices (cars, laptops…)
- Inexpensive production – built from low-cost and readily available materials. DSSC panels are about half the price of Si solar cell technology and in the large production may be 70% cheaper.
- Material specification does not require a high purity level
- High price/performance ratio

6. NANOFIBER APPLICATIONS: BATTERIES

High power density energy storage devices are required in broad range of applications. The lithium-ion battery technology is possessing ability to fulfill demanded performance parameters. However, the performance of conventionally used graphite anode is limiting factor for safety reason, the lithium titanate $Li_4Ti_5O_{12}$ is material which is solution for construction of new type of high rate lithium ion battery. This material can be considered as zero-strain during lithium insertion which emerge solution for safety issue of conventional anodes. Furthermore, as referred in [9] this material prepared as nanoparticles can withstand charging rate capability up to 200C

The electrospinning [7] was recognized as a method for preparation of inorganic materials such as cobalt oxide [8], nickel titanate [9] titanium oxide [10] or $LiCoO_2$ and $LiMn_2O_4$ [11] as well as in fabrication of endless polymeric nanofibers. Inorganic fibers preparation is achieved by spinning of mixture of ceramic precursor in polymer solution and consequential calcination in order to remove polymer template [12], [13].

Due to one-dimensional structures by electrospinning prepared materials were suggested for electrochemical applications as advanced high rate and high power secondary batter. Recently the electrospun spinels like $LiCoO_2$ and $LiMn_2O_4$ [11] were investigated for cathode materials and the spinel lithium titanate ($Li_4Ti_5O_{12}$) for anode [14].

The specific surface area, which is one of the most important parameters for electrochemical devices, can be achieved in same order of magnitude for materials prepared by electrospinning like for nanopowders. The fibrous morphology of electrospun materials contributes to battery performance by reduced internal resistance. High permeability of such material leads to better accessibility of the surface for the electrolyte.

The Nanospider^{TM} technology was demonstrated as feasible to transfer electrospinning into industrial scale production rates. Using this method the lithium titanate was prepared and consequently its electrochemical properties were studied.

EXPERIMENTAL

The spinning solution was prepared by mixing of 16.5 g titanium tetraisopropoxide with 33 ml of acetic acid and 33 ml of ethanol. In addition the stechiometric amount of the lithium acetylacetonate (Li:Ti = 4:5) was diluted in solution. The solution was stirred for 10 min before being added into 82.5 ml of 6 % ethanolic solution of polyvinylpyrrolidone (PVP, Mw=1300000g/mol). The solution was subsequently electrospun using the Nanospider™ technology. The produced precursor nanofibrous layer was calcined in air at 700°C for 4 h.

Precursor and calcinated lithium titanate fibers were analyzed by scanning electron microscope (SEM) The SEM pictures are shown in Figure 9 and 10. The fiber diameter of precursor fibers was found to be in range of 200-800 nm while the diameter of calcined fibers are in range of 100-500 nm, herewith the fiber structure kept unchangeable. By means of higher magnification was observed that the calcined fibers were composed of small grains with size in range of 50-250 nm as shown in Figure 10.

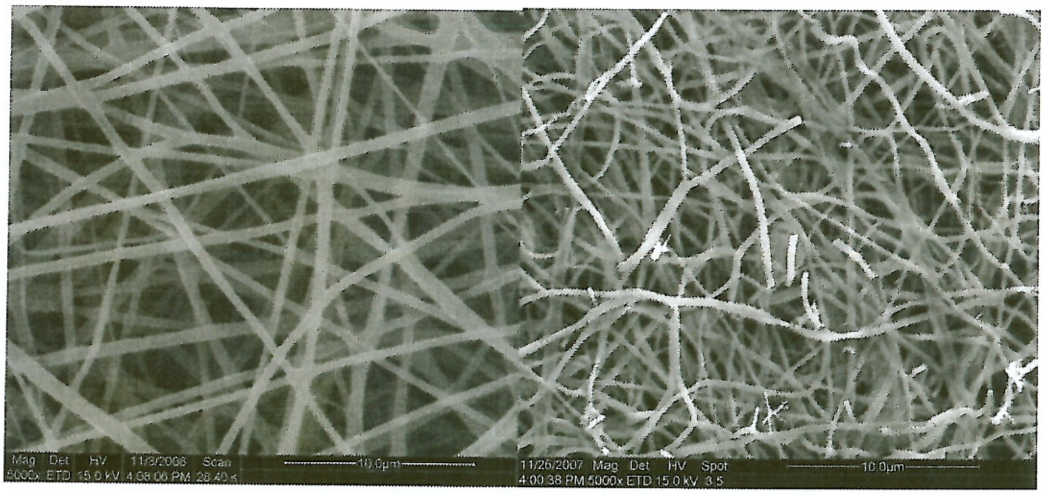

Fig. 9. SEM images of electrospun lithium titanate precursor fibers before (left) and after (right) calcination.

Fig. 10. SEM images of calcined lithium titanate fibers with higher magnification.

Measurement of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature with B.E.T method was used for estimation of specific surface area. It was found to be 40 g/m2.

Crystalline phase of the fibers was identified by X-ray diffraction. Figure 11 shows XRD pattern of the calcined precursor fibers. The diffraction pattern indicated the formation of a pure polycrystalline lithium titanate spinel after calcining procedure.

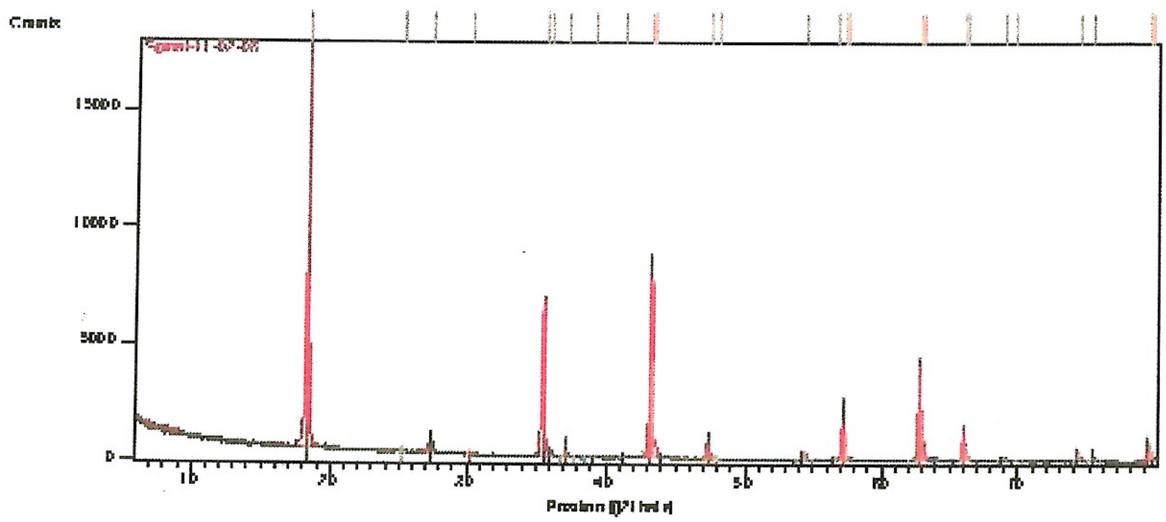

Fig. 11. XRD patterns of $Li_4Ti_5O_{12}$ fibers

The electrochemical performance was investigated using cyclic voltammetry at voltage scan rates 0.1, 0.2, 0.5 and 1 mV/s. The electrode was prepared by casting of slurry of fibrous lithium titanate mixed with 4% aqueous solution of HPC (hydroxypropylcellulose) onto conducting glass by the doctor-blading technique. The electrode was dried in air at 450°C for 30 min. The cyclic voltammetry were measured using lithium wire counter and reference electrode in electrolyte consisted of 1 M $LiPF_6$ in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (volume ratio of 1:1). The electrochemical activity of prepared lithium titanate fibers was evaluated using the cyclic voltammetry at four different scan rate (0.1 - 1 mV/s). The resulted CV is shown in Figure 4. Cyclic voltammograms evidence well-developed spinel structure and excellent charge capacity of 174 mAh/g, which was calculated from anodic branch of CV with the slowest scan rate (0.1 mV/s).

The high specific surface area lithium titanate nanofibers were prepared using Nanospider™ technology. Their physical and electrochemical properties were analyzed and should be emphasized that they exhibit desired properties for construction of advanced high rate lithium-ion battery.

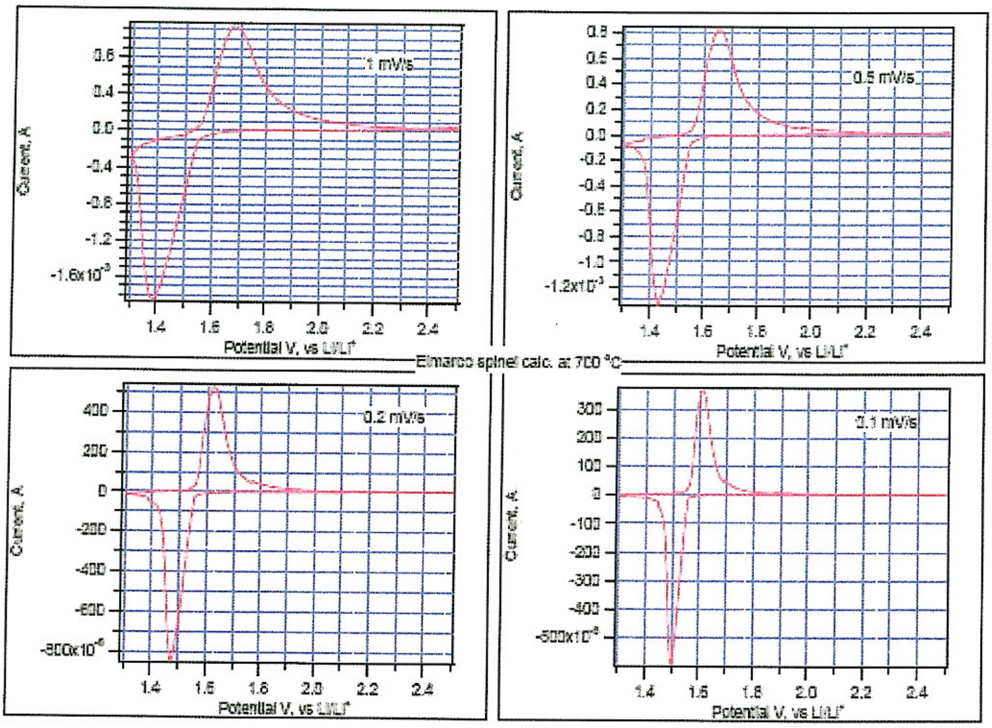

Fig. 12. Cyclic voltammograms of Li insertion in lithium titanate spinel fibers performed in 1M LiPF6 in EC/DMC (1:1, v:v) electrolyte. The voltage scan rates were 1, 0.5, 0.2 and 0.1 mV/s

6. Conclusion

High quality low cost production of nanofiber layers open great opportunities for the development of new products by combining them with quickly evolved nonwoven technologies. The few applications described in the paper demonstrate the need for effective cooperation of nanofiber and "traditional" nonwoven industry experts.

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5. Perspektivy dalšího rozvoje výzkumu a výuky v oboru

Průmyslová výroba nanovlákenných materiálů je v současnosti v období „dospívání" a postupně zvyšuje potřebu mezioborového výzkumu v oblasti poznání podstaty technologických procesů, kterou z velké části naplňuje základní akademický výzkum. Současně však přináší i zásadní zvýšení potřeby zkoumání a pochopení specifických problémů spojených se zvětšováním výkonu výrobních procesů a zařízení, s konzistentností kvality vyráběných produktů a s růstem ekonomické efektivity tohoto nového průmyslového odvětví. To v konečném důsledku rozhoduje o tom, jestli se příslušný produkt dostane do reálného života.

Příkladem zapojení uchazeče do dalšího výzkumu v tomto oboru je projekt TA04011086 „Optoelektronický systém pro řízení kvality výroby nanovlákenných materiálů" zaměřený na výzkum a vývoj zařízení, které umožní zavedení zpětné vazby do technologie beztryskového elektrostatického zvlákňování. Cílem je zvýšení kvality a efektivity výroby nanovlákenných materiálů, které očekávají uživatelé výrobních linek. Projektový tým je výrazně mezioborový a zahrnuje výzkumníky z praxe (Elmarco) a odborníky z oblasti elektrostatiky, optiky, fotoniky, zpracování obrazu a mechaniky tekutin (TUL). Kromě významu pro průmysl výroby nanovláken má tento projekt i velký edukativní význam, protože je výbornou příležitostí pro zapojení studentů jak do vývoje a testování systému, tak i do jeho zavedení do průmyslu v průběhu jejich praxe ve firmě.

Průmyslové aspekty výzkumu nanovlákenných materiálů a produktů si budou vyžadovat další rozšiřování edukativních aktivit na všech úrovních vzdělávání. Uchazeč je zapojen do projektu CZ.1.07/2.3.00/45.0011 EDUTECH, v rámci kterého garantuje dva kurzy zaměřené na zapojení talentovaných středoškoláků do studia optických vláknových senzorů a nanomateriálů. Na TUL přenáší předmět „Inovace a podnikání v nových technologiích" a připravuje zavedení dalšího předmětu „Průmyslová výroba nanomateriálů". Na mezinárodní úrovni pokračuje v pravidelné výuce na North Carolina State University v rámci kurzu „Micro and Nanofiber Production Fundamentals". Velký význam má další rozvoj konferenčních aktivit, které oslovují širší odbornou veřejnost z akademické i podnikatelské sféry. Příkladem je letošní celosvětová konference s touto tematikou v Liberci - „Nanofibers, Applications and Related Technologies – NART 2015".

Vize dalšího vědeckého zájmu uchazeče se opírají o propojení zkušeností z oblasti výzkumu optických vláknových senzorů a nanovlákenných materiálů. Ve stadiu ověřování principu je pilotní optický vláknový systém, který poslouží jako základ výzkumu nových senzorů fyzikálních, chemických a biologických veličin založených na využití funkcionalizovaných nanovláken jako citlivých prvků. Kromě nových zajímavých vědeckých témat bude prostorem pro zapojení talentovaných studentů formou bakalářských, diplomových a doktorských prací a pro rozšíření nabídky mezioborových studijních předmětů.

6. Závěr

Cílem habilitační práce bylo poukázat na přínosy uchazeče ve výzkumu a vývoji průmyslové technologie výroby a aplikací nanovlákenných materiálů, založené na beztryskovém elektrostatickém zvlákňování objeveném na Fakultě textilní Technické univerzity v Liberci. Publikace, které tvoří habilitační práci, jsou seskupeny to tří témat a demonstrují:

- Příspěvek v oblasti vývoje průmyslové technologie,
- Příspěvek v oblasti využití technologie pro filtrační aplikace,
- Příspěvek ve vývoji dalších aplikací, které mají vysoký komerční potenciál a jsou na prahu průmyslové výroby.

Několikaletá výzkumná, vývojová, pedagogická a popularizační práce uchazeče přispěla k tomu, že v současnosti je technologie beztryskového elektrostatického zvlákňování respektována jako první volba výrobců materiálů pro filtraci a další aplikace netkaných textilií, kteří usilují o zachování svého postavení na trhu a využívají k tomu zásadní inovace. Vymezení této technologie vůči alternativním metodám výroby mikro a nanovláken přispělo k rychlejšímu soustředění výzkumu na oblasti, ve kterých je elektrospining zatím nejlepší. To platí především pro aplikace vyžadující vysokou rovnoměrnost nanovlákenné vrstvy a úzkou distribuci průměrů nanovláken, jako je například vzduchová filtrace. Intenzivní výzkum technologií a aplikací nanovláken, který v současnosti pokračuje, zřejmě přinese další specializaci, zohledňující specifika jednotlivých technologií a aplikačních oblastí, jak z pohledu technických parametrů produktů, tak z pohledu ekonomiky jejich výroby. I když beztryskový elektrospining patrně nebude v blízké budoucnosti jedinou technologií na trhu, jeho historický význam pro vznik nového „nanovlákenného" odvětví zůstane nezpochybnitelný.

7. Seznam publikací a pedagogických prací uchazeče k tématu habilitační práce

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