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Industrial Production
Technology for Nanofibers

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1. Introduction

Electrospinning methods for creating nanofibers from polymer solutions have been known for decades (Kirichenko et al., 2007, Ramakrishna et a., 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). 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. 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 (Proceedings, 2009). Inorganic/ceramic nanofibers attract growing interest as materials for energy generation and storage (solar and fuel cells, batteries), and catalytic materials (Kavan & Grätzel, 2002, Duchoslav & Rubacek, 2008, Rubacek & Duchoslav, 2008, Bognitzki et al., 2001, Guan et al., 2003). 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 the technology has matured to this stage.

2. 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 (Bognitzki et al., 2001, Taylor & Van Dyke, 1969, Doshi & Reneker, 1995, Thompson et al., 2007, Shin et al., 2001, Yu et al., 2006, Hohman et al., 2008). 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., 2008). Secondary splitting of the liquid polymer streams can occur also (Kirichenko et al., 2007), 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) (Reneker, 2009).

a   **b**
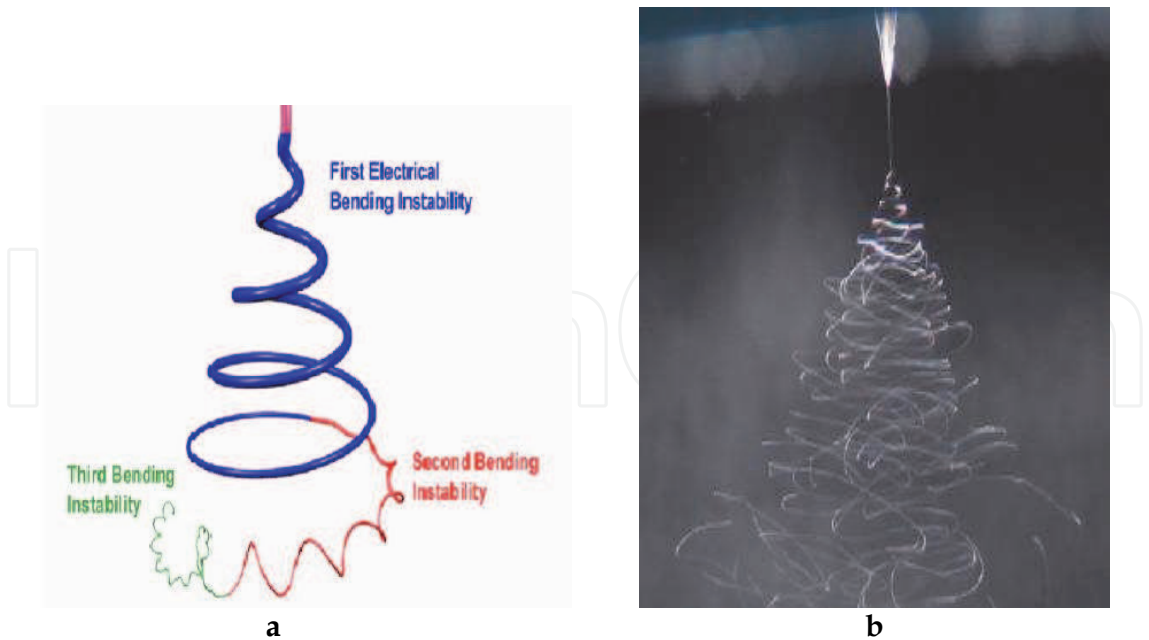
(Courtesy of Darrell Reneker, University of Akron)

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

A comprehensive analysis (electrohydrodynamic model) of the fiber formation mechanisms published by (Hohman et al., 2008) 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.
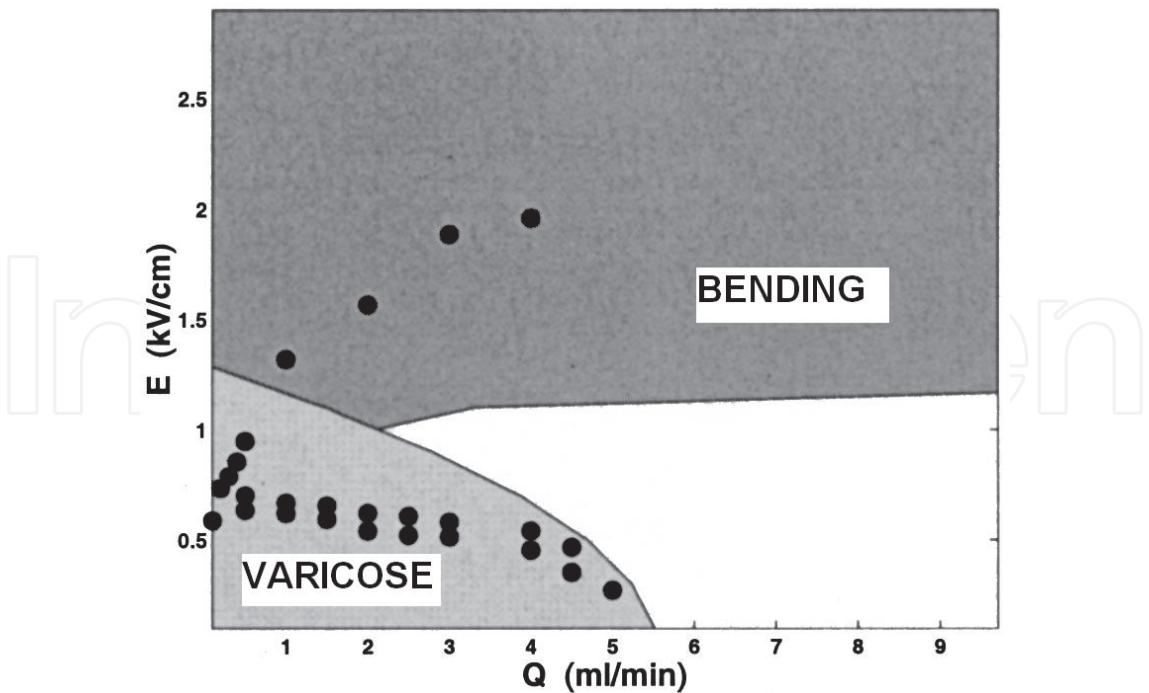

Fig. 2. Operating diagram for a PEO jet. The upper shaded region shows the onset of the whipping instability, the lower one shows the onset of the varicose instability (Hohman et al., 2008).

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 Figure 3, 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.
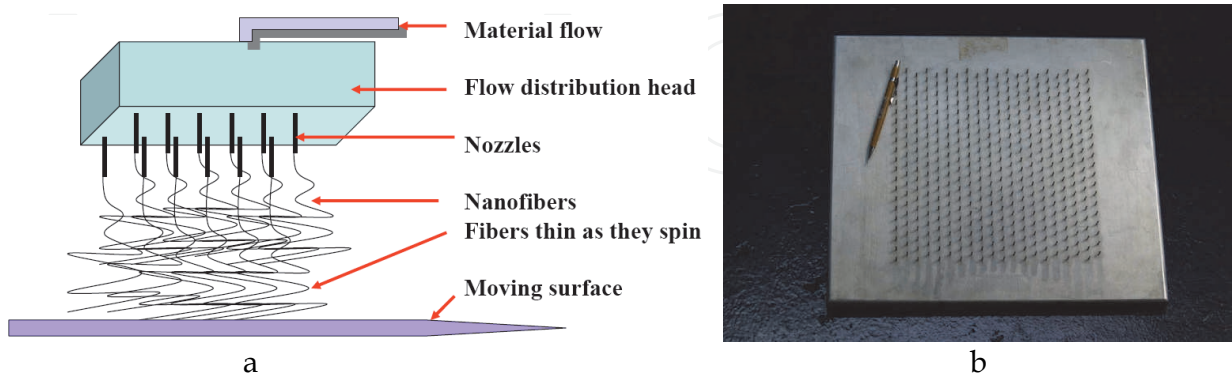

| a | b |

Fig. 3. Schematic (a) and photograph (b) of a multi-nozzle spinning head by NanoStatics (NanoStatics, 2007).

Figure 4 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.
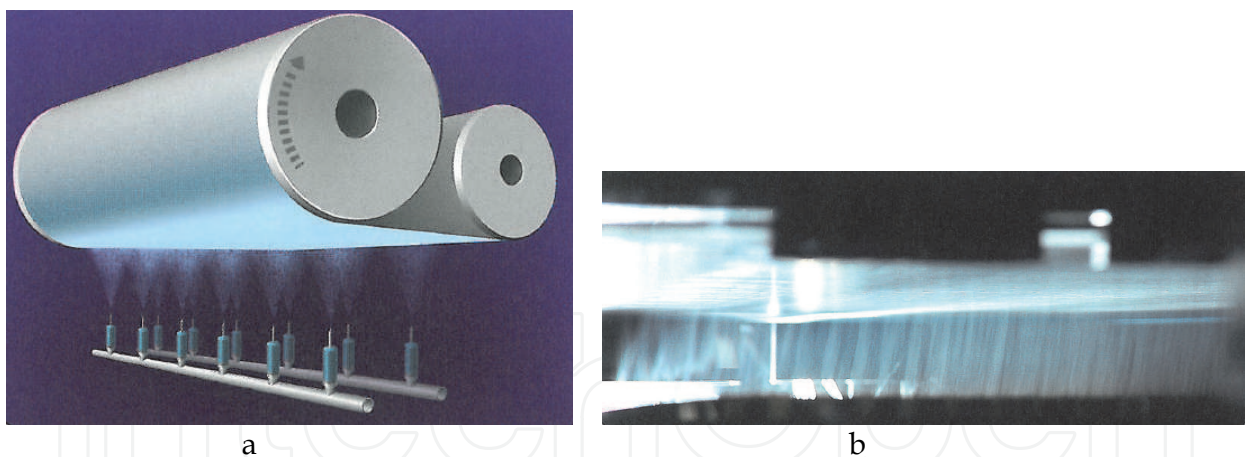

| a | b |

Fig. 4. Schematic (a) and photograph (b) of a multi-nozzle spinning head by TOPTEC (TOPTEC, 2011).

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., 2008) 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

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

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

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

where E_0 is electric field strength, γ – surface tension.
The relationship between angular frequency ω and wave number k is in Figure 5, 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

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

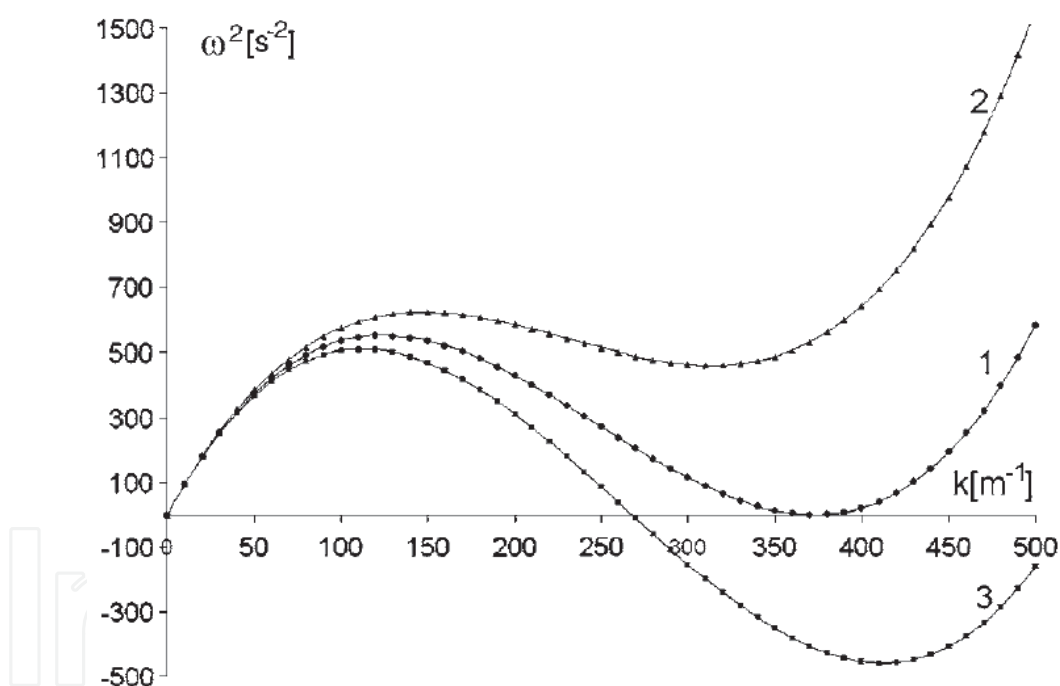exponentially grows, which leads to an instability.

Fig. 5. 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 094x10⁶ V/m, 2: E=2.4x10⁶ V/m, and 3: E=2.5x10⁶ V/m (Lukas et al., 2008).

Critical field strength can then be expressed

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

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 6).
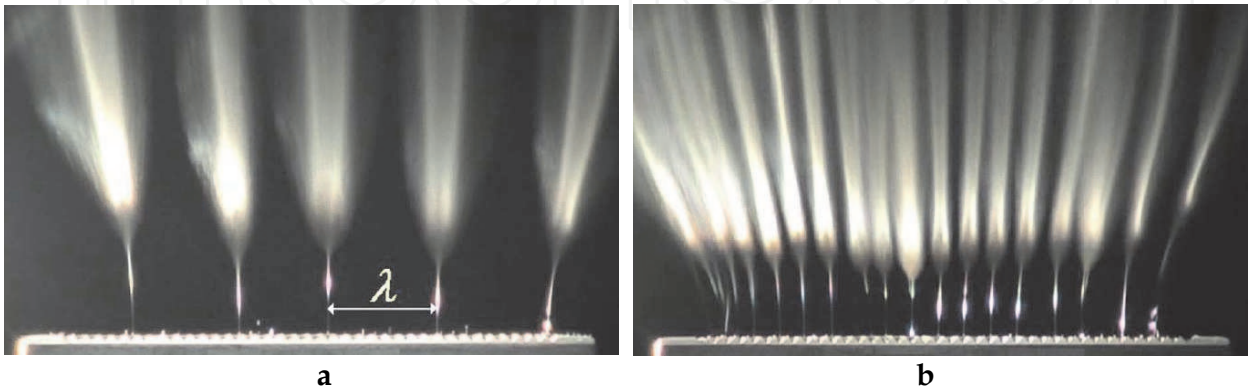
$$\lambda_c = 2\pi / k_c = 2\pi a \tag{5}$$

and

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

a is the capillary length

$$a = \sqrt{\gamma / \rho g} \tag{7}$$

a   b

(Courtesy of David Lukas, Technical University of Liberec)

Fig. 6. Free liquid surface electrospinning of Polyvinyalcohol at 32 kV (a) and 43 kV (b).

3. Technical realization

3.1 Description of the nozzle-less technology

The simplest realization of the nozzle-less electrospinning head is in Figure 7a. 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

a   b

Fig. 7. Free liquid surface electrospinning from a rotating electrode (a) and various types of spinning electrodes (b).

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 7b). However, the drum type is still one of the most productive.

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

3.2 Alternative 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 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.

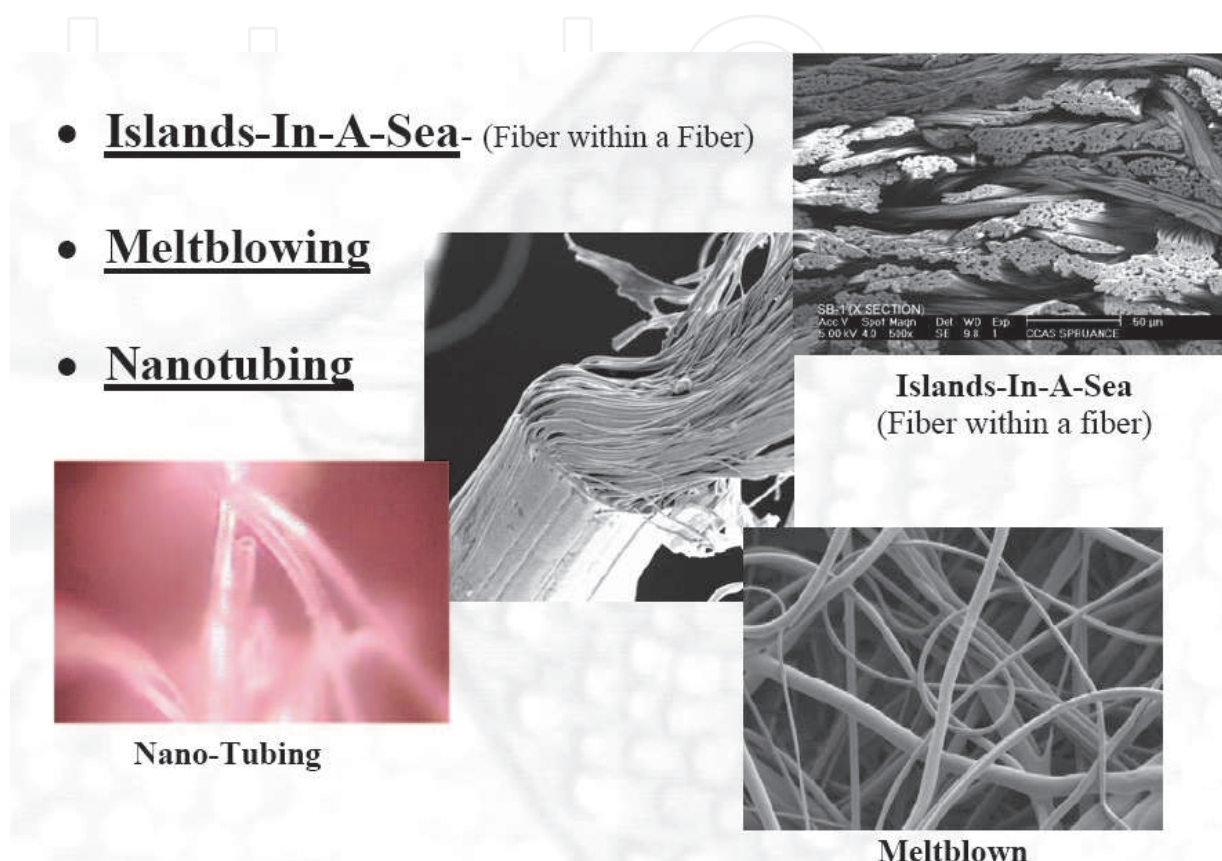Figure 8 shows the extrusion methods being developed by Hills Inc. (HILLS, 2011).

Fig. 8. Fibers made by extrusion methods (HILLS, 2011).

Centrifugal forces for elongation of liquid polymer into thin fibers are used in the approach developed by (Dauner et al., 2008). The productivity of the process they claim is high (up to 1000 cm^3/m.hr), however, the fiber diameter distribution and homogeneity of the deposited nanofiber layer is not at the levels achieved by electrospinning.

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 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).
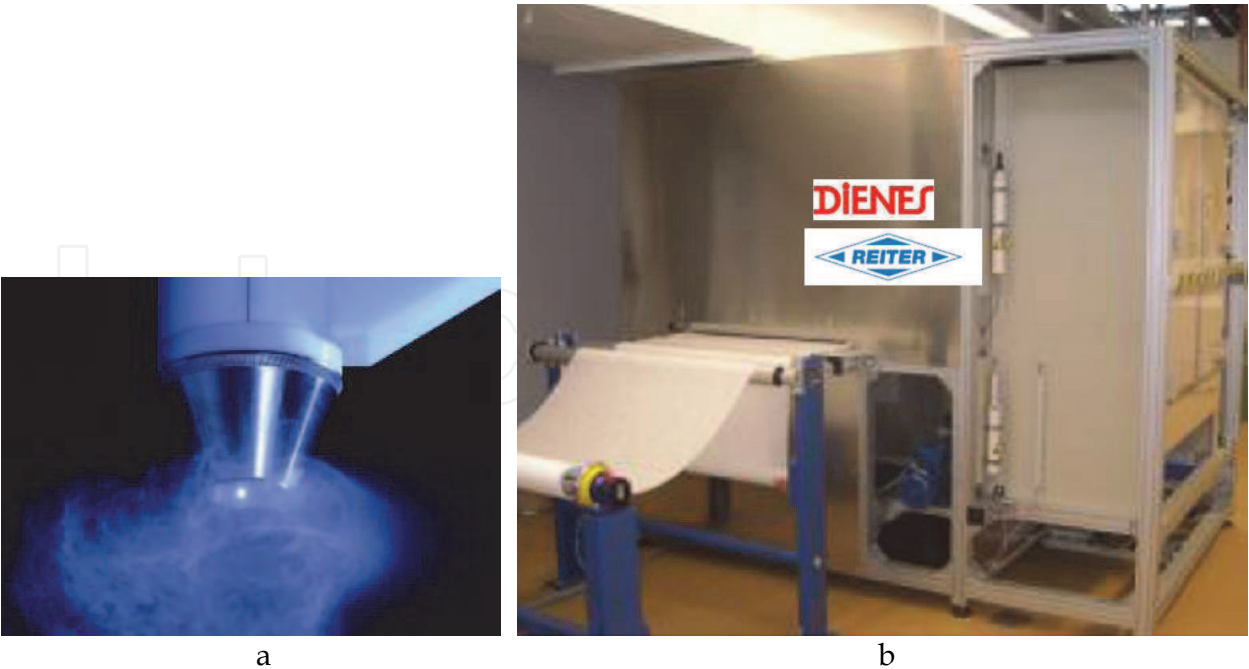
<center>a</center> <center>b</center>

Fig. 9. Centrifugal spinning head (a) and a pilot production line by Dienes/Reiter (b) (Dauner et al., 2008).

	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

Table 2. Nanofiber Production Methods.

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 10.

Fig. 10. Nozzle-less production electrospinning line (Nanospider™).

3.3 Performance of the technology

In addition to productivity (or throughput) of the production line, individual industrial applications require certain production consistency. Petrik & Maly illustrated 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 (Petrik & Maly, 2009). 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 11. 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).
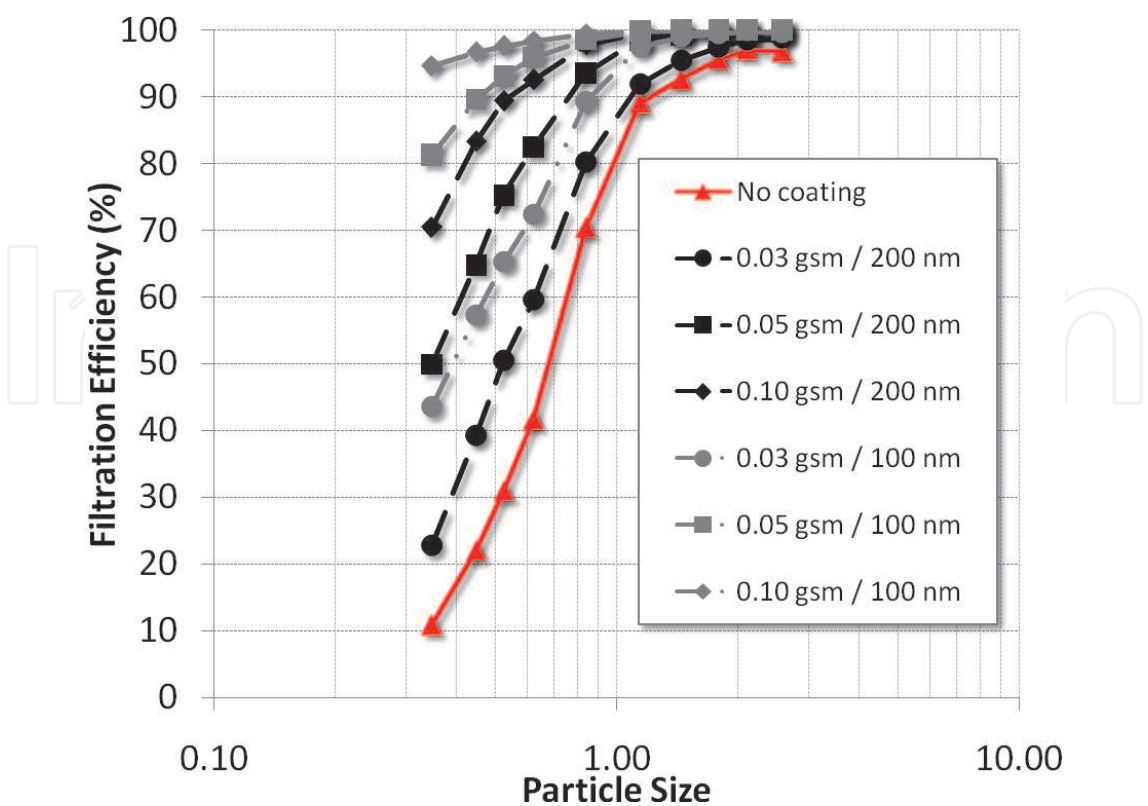
Fig. 11. Filtration efficiency of nanofiber media samples.

Pressure drop for various coatings at 10 m/min face velocity						
Substrate	Basis Weight	NF Diameter	Filtration Efficiency		Pressure Drop	
	(g/m²)	(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%

Table 3. Properties of nanofiber filtration media samples shown in Figure 11.

For production technology tests, 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 cm², flow rate 50 l/min.

In Figure 12, 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 exhibits the value of the basis weight of the nanofiber layer, shown in Figure 13.
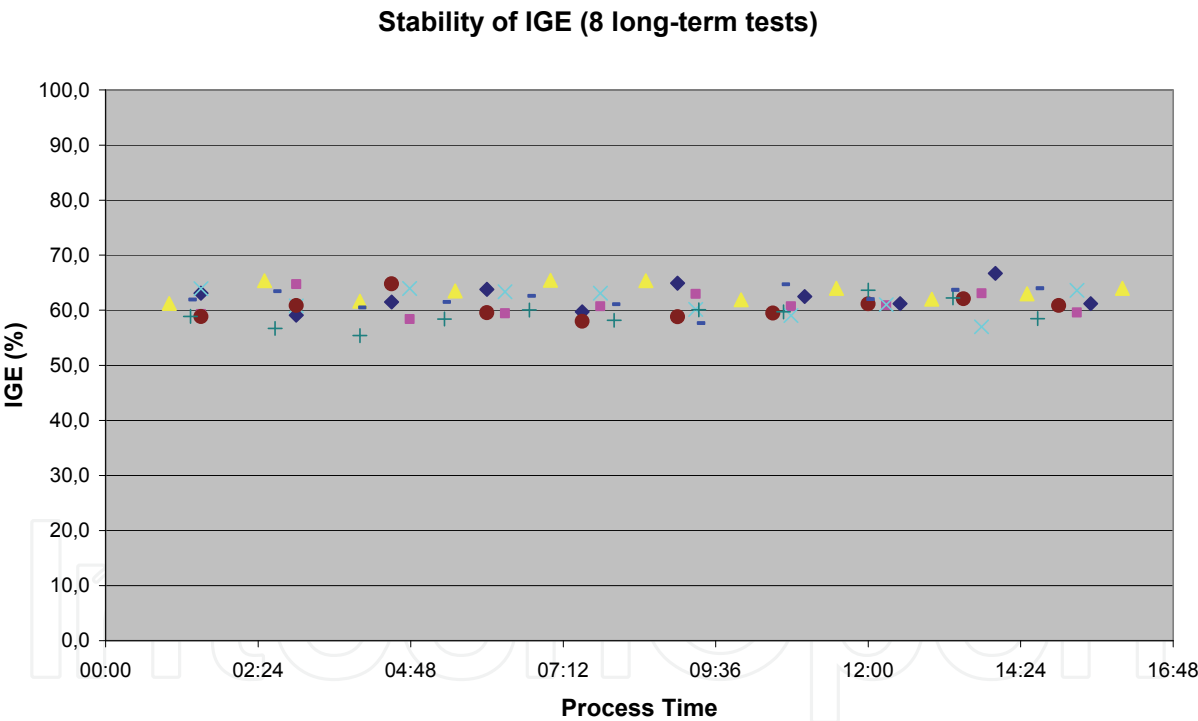
Fig. 12. Stability of initial gravimetric filtration efficiency of the media produced at the industrial nozzle-less electrospinning equipment.
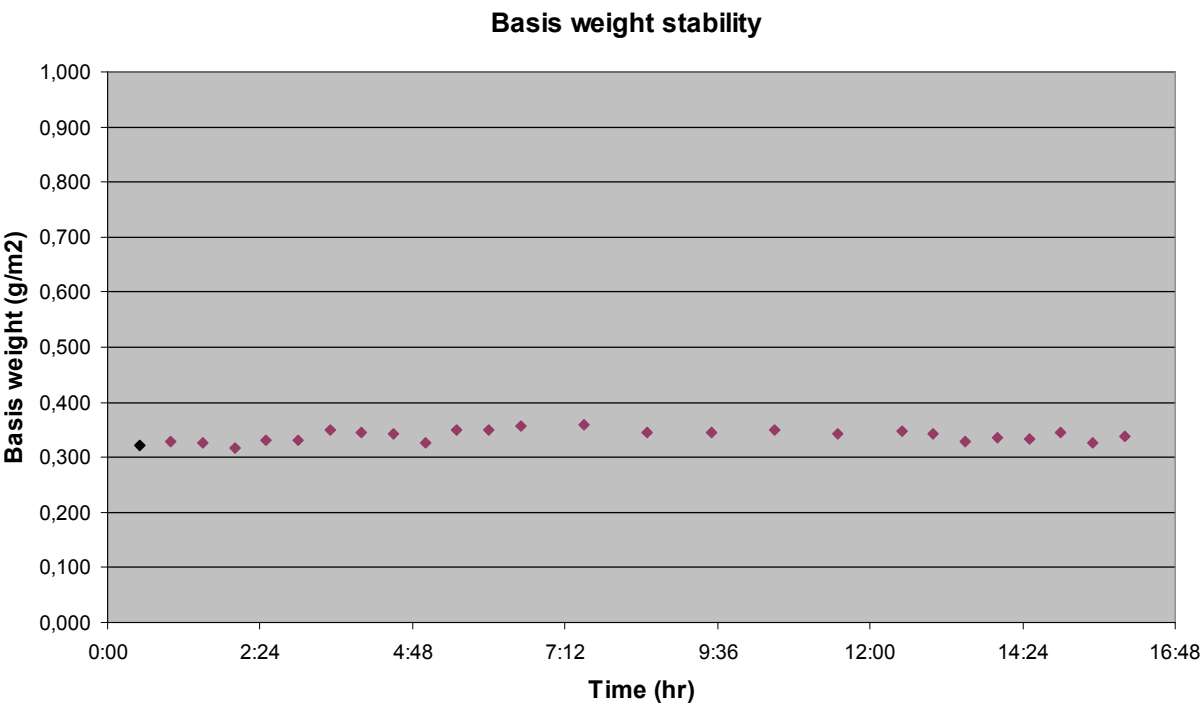
Basis weight stability

Fig. 13. 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 14. Pressure drop was measured in 10 evenly distributed points at a cross section of the substrate belt.
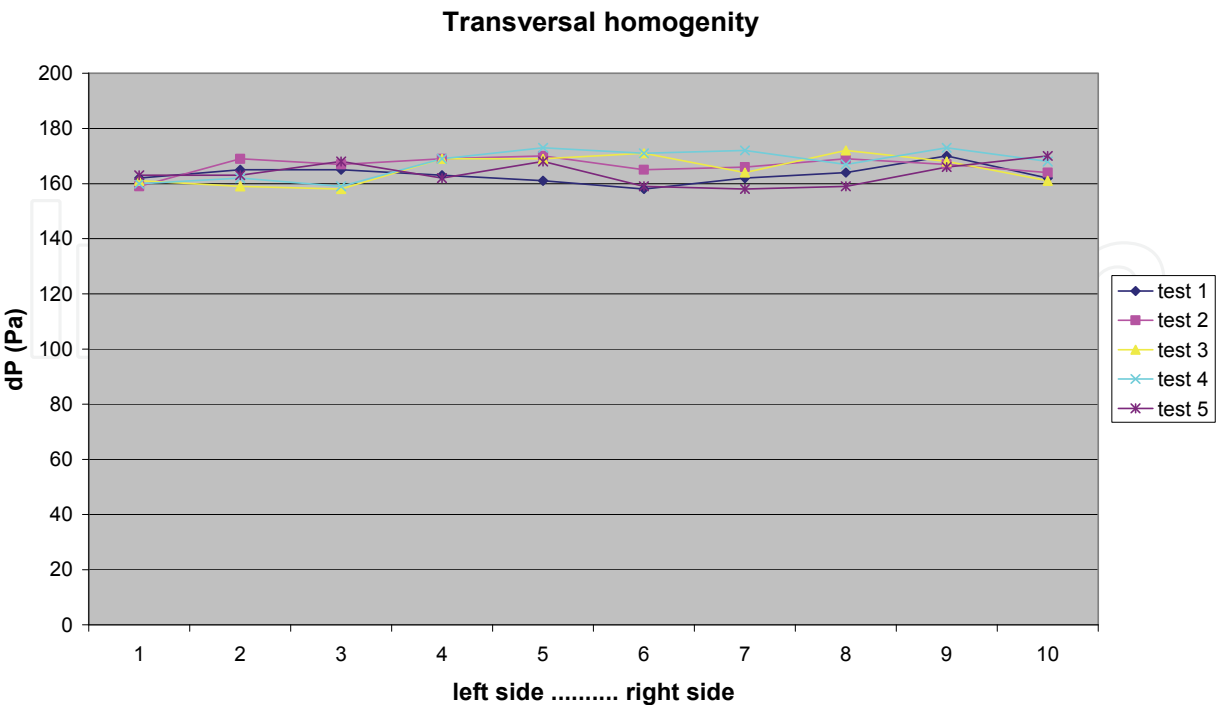
Transversal homogenity

Fig. 14. 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 15.
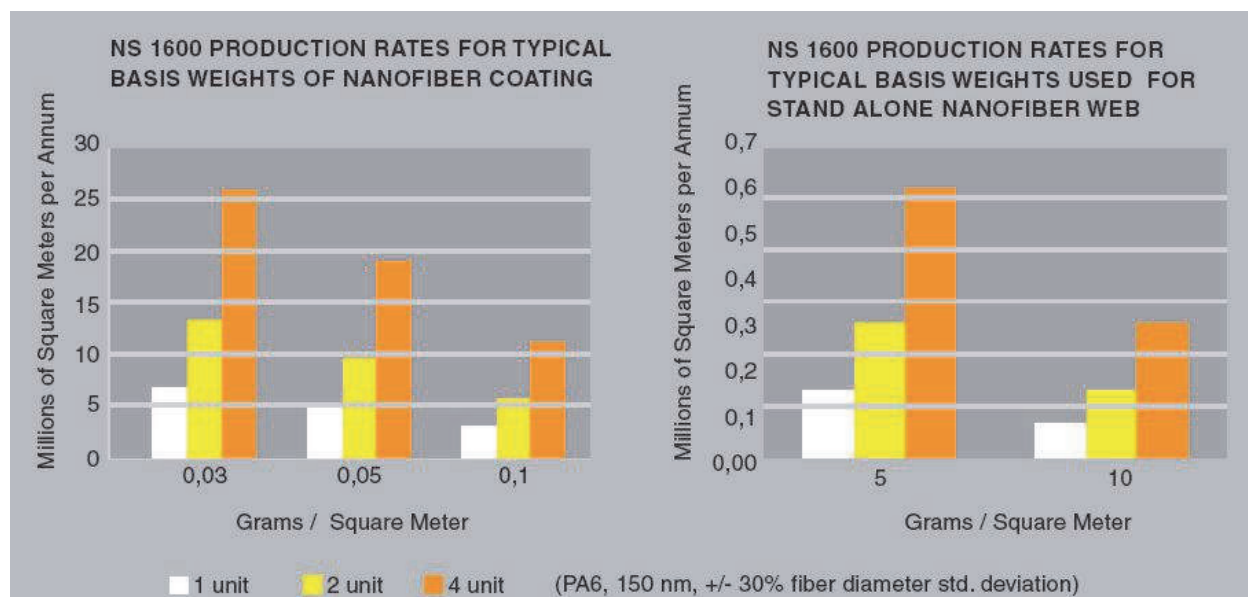

Fig. 15. Production capacity of the nozzle-less electrospinning line with Polyamide 6.

4. 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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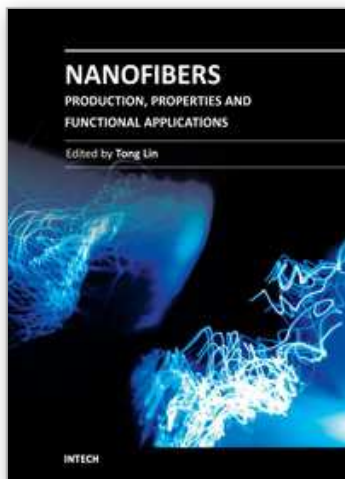
Nanofibers - Production, Properties and Functional Applications

Edited by Dr. Tong Lin

As an important one-dimensional nanomaterial, nanofibers have extremely high specific surface area because of their small diameters, and nanofiber membranes are highly porous with excellent pore interconnectivity. These unique characteristics plus the functionalities from the materials themselves impart nanofibers with a number of novel properties for advanced applications. This book is a compilation of contributions made by experts who specialize in nanofibers. It provides an up-to-date coverage of in nanofiber preparation, properties and functional applications. I am deeply appreciative of all the authors and have no doubt that their contribution will be a useful resource for anyone associated with the discipline of nanofibers.

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