

Production Technology for Nanofiber Filtration Media

M. Maly and S. Petrik

Elmarco s.r.o.

V Horkach 76/18, CZ-46007 Liberec, Czech Republic, stanislav.petrik@elmarco.com

ABSTRACT

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

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.

Keywords: nanofibers, electrospinning, production, technology, filtration

1 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.

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 [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].

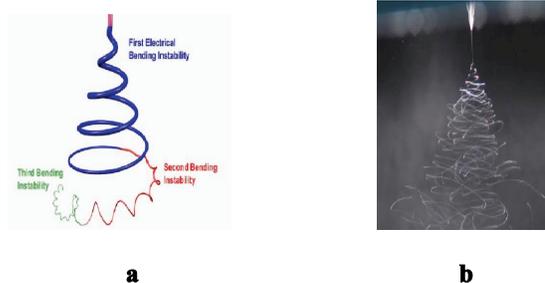


Figure 1. The path of an electrospinning jet (a – schematic, b – stroboscopic photograph).

(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

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

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

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

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

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

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

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 (Figure 2).

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

and

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

a is the capillary length

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

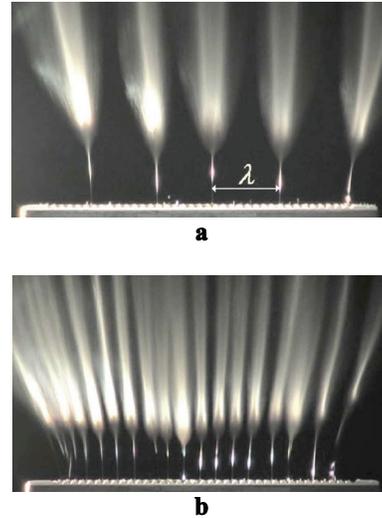


Figure 2. Free liquid surface electrospinning of Polyvinylalcohol at 32 kV (a) and 43 kV (b).
(Courtesy of David Lukas, Technical University of Liberec)

3 TECHNICAL REALIZATION AND DISCUSSION

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.

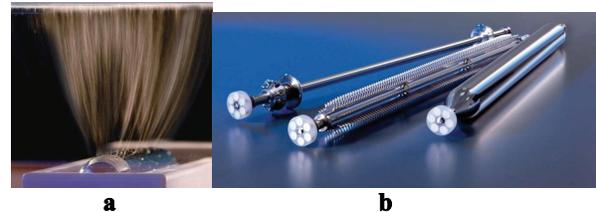


Figure 3. Free liquid surface electrospinning from a rotating electrode (a), and various types of spinning electrodes (b).

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™ machine is in Figure 4.



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

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 5. 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).

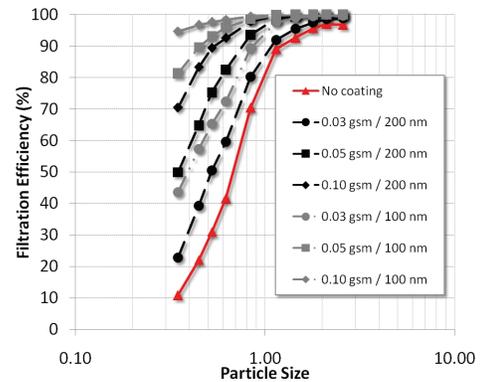


Figure 5. Filtration efficiency of nanofiber media samples

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 6, 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.

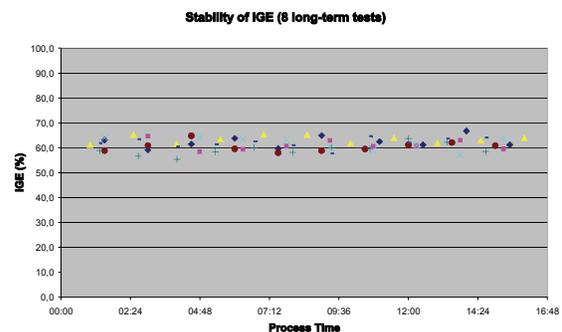


Figure 6. Stability of initial gravimetric filtration efficiency of the media produced at the industrial nozzle-less electrospinning equipment.

Production capacity of the industrial electrospinning line for Polyamide 6 is illustrated in Figure 7.

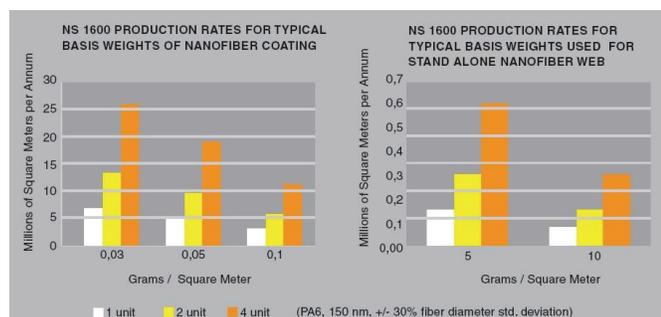


Figure 7. Production capacity of the nozzle-less electrospinning line with Polyamide 6.

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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