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Production of Poly(vinylalcohol) Nanoyarns Using a Special Saw-like Collector

Abstract
This work introduces an electrospinning method for laboratory-scale production of nanofibrous materials from polyvinylalcohol (PVA) nanofibres. A procedure for the subsequent production of twisted yarns from the aligned nanofibrous strand is introduced as well. Both needle and needleless electrospinning variants were employed. Mechanical properties of the nanoyarns produced were tested using a VIBRODYN 400 and their morphology was investigated by light and electron microscopy. The work also introduces a simple analysis of the field strength that causes the prevailing unidirectional fiber deposition between neighbouring lamellae of a special saw-like collector. The field strength analysis was carried out both analytically and by modelling based on the software COMSOL Multiphysics.

Key words: *needle-less electrospinning, aligned nanofibers, nanoyarns.*

Introduction

The leading technology for the massive production of nanofibres is electrospinning, a process that forms nanofibres from polymer solution or polymer melts using electrical field gradients. It is expected that nanofibre yarns, similar to nanofibre layers, will find applications in high value-added fields such as composites, filtration media, gas separation, sensors, biomedical engineering, etc. In recent years, researchers have explored novel mechanical and electrostatic mechanisms to better control the electrospinning process. The effort is, among others, focused on collecting ordered yarns aiming at further improvements in yarn morphology, mechanical properties, linear density and fibre orientation/twist. Nanoyarn producing technologies can be divided into the following groups.

The first trial to make nanofibrous continuous yarns used a rotating disc electrode and was done by Formhals *et al.* [1 - 3]. Next attempts to employ various kinds of rotating collectors were made by Huang [4], who collected fibre bundles onto the sharp edge of a thin rotating wheel using an auxiliary electrode. Zussman *et al.* applied a wheel-like bobbin as a collector to position and align individual polymer nanofibres into parallel arrays [5]. Fennessey used a high speed rotating take-up wheel [6], while Dalton [7] and Liu [8] suspended electrospun nanofibres between two grounded plate electrodes while rotating one of them. Wu *et al.* applied three parallel electrodes in the vicinity of a rotating-drum collector to ensure more narrowly-aligned nanofibre bundle [9]. Dabirian *et al*. [10] used a negative charged bar to place the nanofibrous strands created by electrospinning on the surface of a rotating drum. Bazbouz and Stylios [11] employed two parallel circular plates standing upright to obtain three-dimensionally aligned nanofibre bundle and yarn.

Methods for yarn production primarily based on the application of an electric field to twist fibres have been introduced by Fennessey and Farris [6, 12], who linked and twisted unidirectional tows of electrospun nanofibres into yarns using an electric twister. Li *et al.* [13 - 16] and Pan [17] developed a method of conjugate electrospinning from oppositely charged electrospun nanofibres. Okuzaki [18] reported on centimetre-long fibres spontaneously electrospun into yarns vertically on the surface of a flat collector. Sarkar *et al.* produced highly-aligned nanofibre array through the biased AC electrospinning process [19]. Dabirian *et al.* employed two differently charged nozzles and a collector travelling through the air to form yarn continuously [10]. A study detailing a theoretical analysis of the distribution of the electrostatic field forming around spinning points was presented in [28].

Other works used fluid motion to twist nanofibres into yarns. Scardino applied an air vortex spinning method to impart twist to fibres, forming a core filament spun yarn [20]. In Yong's work an air turbulence twister was applied to increase cross linking between nanofibres and to apply twist to them [21]. Kataphinan *et al.* refer to collecting nanofibres off the surface of non-wetting liquids [22]. The electrospinning of a continuous fibre bundle yarn onto a liquid reservoir and then collecting the fibres has also been reported by Liu [23].

Furthermore self-bundling and self-assembling electrospinning methods of producing continuous polymer nanofibre yarns were described by Wang *et al.* [25] and also by Mondal *et al.* [25].

In this paper a novel electrospinning set-up is introduced to provide a simple method for generating aligned electrospun fibre yarn with lengths of about 50 cm. Compared to common electrospinning setups, a special saw-like collector is used. The purpose of the collector shape chosen is to align nanofibres in the space between the neighbouring lamellae by means of electric field distribution in the vicinity of the collecting device. We also developed a simple theoretical approach to explain the prevailing parallel orientation of pieces of the electrospinning jet during its looping motion in-between neighbouring collector lamellae. COMSOL Multiphysic software was used to reveal details of our analytical approach.

Material and methods

It is common for electrospun nanofibres to be deposited on a homogeneous metallic planar collector. Electric charges are transmitted together with electrospinning jet force nanofibres to form a random mesh. Our approach to produce short nanofibrous yarns is based on the employment of a special saw-like collector. Such a collector causes the inhomogeneous distribution of the field strength in its vicinity. Therefore nanofibres are preferentially deposited in strands on lamella tips with a parallel alignment between them. The arrangement of nanofibrous strands due to the field distribution is described in the theoretical part of the work.

Materials

Water soluble polyvinylalkohol SLOVIOL (PVA) from Chemicke zavody Novaky (Slovakia) was used with an original concentration of 16 wt%. The mean molecular weight of this polymer is 130000 g/mol. Polyvinylalkohol was diluted in distilled water to a final concentration of 12 wt%.

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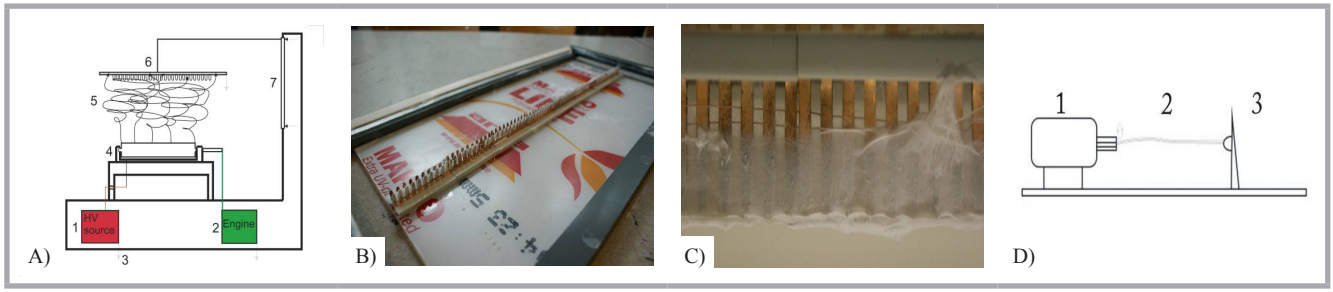

Figure 1. *(A) Nanospider™ technology, 1 high voltage source, 2 engine, 3 grounding, 4 roller in the bath of a polymer solution, 5 nanofibres, 6 collector, 7 frame for regulation of the distance between the roller and collector, (B) Special saw-like collector. (C) Detail view of saw-like collector covered by nanofibrous layer (D) Twisting device, 1 engine, 2 nanofibrous bundle, 3 fixing frame.*

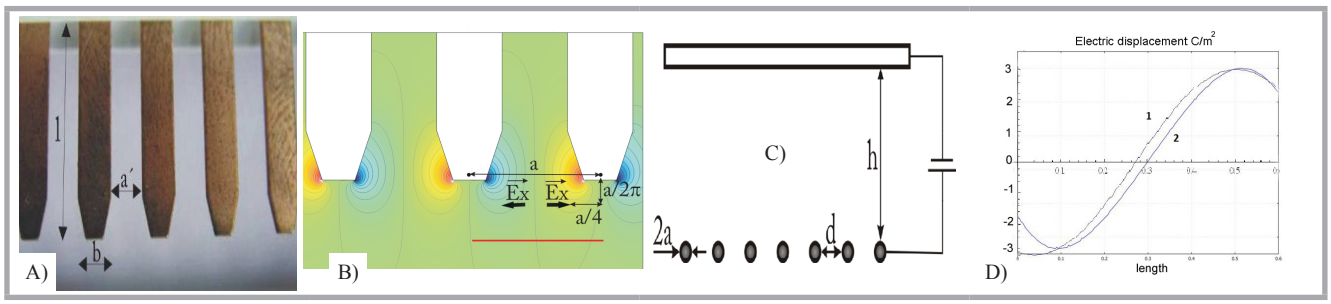

Figure 2. *(A) Lamellae of the special saw-like collector, l = 12 mm, a′=3 m, b = 3 mm. COMSOL Multiphysic simulation: (B) Field strength x-component near two lamellae of the special saw-like collector, (C) A model of the saw-like collector, consisting of a grid of parallel and equidistant metallic rods. (D) Electrostatic strength component E_x along an abscissa in figure part B that is at a distance of $z = a/(2\pi)$ apart from the lamellae tips. Theoretical prediction obtained using Equation (3) is curve 2, COMSOL plotted outputs is line 1.*

Electrospinning set-ups

Experiments were carried out using a needleless electrospinner - Nanospider. The needleless variant employed a cylindrical spinning electrode with a diameter of 14 mm and length of 83 mm that rotates slowly around its horizontally oriented axes in a bath of polymer solution, with a length of 100 mm, width of 30 mm and height of 15 mm, see ***Figure 1.A***. This arrangement follows the idea of Nanospider™ introduced by Jirsak *et al.* [26]. The collector used, composed of cooper lamellae with a vertical length of 11 mm, width of 1 mm, thickness of 3 mm and distance between neighboring lamellae of 3 mm, is depicted in ***Figure 1.B*** and ***Figures 2.A, 2.B***. The distance between the rotating cylinder and collector was 120 mm. The polymer solution was placed on the roller surface as a consequence of its rotation. Taylor cones, as roots of a great number of electrospinning jets, rose from the top of the coated roller surface. Jets were attracted by a special saw-like collector. The collector was grounded while the roller was connected to the positive pole of a 300 Watt High Voltage DC Power Supply; model number PS/ER50N06.0-22; manufactured by Glassman High Voltage, INC. (USA) with output parameters: 0 - 50 kV, 6 mA.

All experiments were carried out at an ambient temperature of 21 ± 2 °C and relative humidity of 40 ± 2%. The voltage used for experiments with PVA was 45 kV. Polyvinylalcohol nanofibres were spun using the needlelees roll apparatus for 15 minutes. ***Figure 2.D*** shows two curves: The first is the theoretical prediction obtained using ***Equation 3*** and the last represents outputs from the program COMSOL MULTIPHYSIC. A normalised curve of the amplitude is plotted as line number 2 in ***Figure 2.B***. Both curves are similar.

Twisting a yarn

The nanofibrous layer deposited on the top of the saw-like collector was taken down. The head of the oriented nanofibrous strand was attached to the twisting device and the tail was clamped by a fix frame. Twist was obtained using the engine in the twisting device run with a rotation speed of around 750 r.p.m for 1 minute. This apparatus is shown in ***Figure 1.D***. Oriented nanofibrous materials of 50 cm length produced using the electrospinning set-ups described equipped with the special saw-like collector were subsequently twisted.

Mechanical characterisations of yarns

The field strength distribution around the saw-like special collector composed of lamellae was investigated numerically using the electrostatic application mode available in COMSOL Multiphysic (***Figure 3***).

Five samples of yarns were used for mechanical testing. The clamping length of each sample test was 1 cm. The strength of individual yarn pieces was measured using a VIBRODYN 400 dynamometer in the testing mode at a constant deformation rate. The device was connected to a VIBROSKOP 400, which enabled to measure the linear yarn density using mechanical oscillation frequency. The software provided automatic evaluation of yarn linear density (fineness), strength, tenacity and relative strength. The fineness of nanofibrous yarns was 394 ± 156 tex, elongation 50.37 ± 7.39 %,

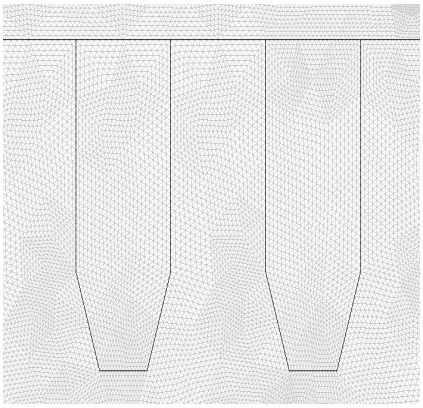

Figure 3. *Lagrange – Quadratic mesh elements and mesh geometry.*

Table 1. Elongation, ultimate tensile strength and relative strength of nanofibrous yarns of different values of yarns fineness.

Yarns fineness, tex	Elongation, %	Strength, cN	Relative strength, cN/tex
221	38,14	272,52	1,23
229	52,66	354,98	1,55
474	54,57	577,45	1,22
505	59,74	573,26	1,14
539	46,77	654,41	1,21

strength 487 ± 146 cN and relative strength 1.27 ± 0.14 cN/tex. There is only occasional information about the strength data of nanofibrous nanoyarn in literature. Ultimate tensile strain and strength values of the nanoyarn produced by us are presented in ***Table 1***.

Theory and mathematical simulation

The analysis of the field distribution around the special saw-like collector was simplified to a two-dimensional model of the grid of parallel and equidistant metallic rods, see ***Figure 2.C***. All rods have the same electric potential and are located perpendicularly to the saw plane in the centers of the lamellae edges, as shown in ***Figure 2.C***. Analysis of the electrostatic field distribution will be restricted to the plane of the saw, i.e. (x,z) plane. The x-axis is horizontal, while the z one is vertical. The electrostatic potential of the problem, $\varphi(x,z)$ is proposed to be in the shape of a Fourier series, as introduced by Feynman *et al.* [27].

$$\varphi(x,z) = E_0 z + \sum_{n=1}^{\infty} F_n(z)\cos\frac{2\pi n x}{a} \qquad (1)$$

where a is the spacing between neighboring nodes/lamellae and n denotes a particular harmonic component of the electrostatic potential φ, while $F_n(z)$ are unknown functions of coordinate z. The potential has to fulfill the Laplace equation $\partial\varphi(x,z)/\partial x + \partial\varphi(x,z)/\partial z = 0$ that holds in the space outside electric charges. The substitution from the Fourier series into the Laplace equation allows to determine functions $F_n(z)$'s as follows

$$F_n(z) = A_n \exp\left(-\frac{2\pi nz}{a}\right) \qquad (2)$$

The n-th harmonic Fourier component of the field decreases exponentially with increasing distance z from the lamella edge. The decays are determined by parameter n. The zero potential component ($n = 0$) is without any decay and the first one ($n = 1$) diminishes in the slowest manner. At a distance equal to $a/(2\pi)$ the first harmonic component prevails, while components with $n > 1$ diminish rapidly. The electrostatic field is nearly uniform at distances only a few times greater than a away from the collector, i.e., $\varphi_0(z) = E_0 z$, meaning that the oscillating terms ($n > 0$) are negligible at these distances.

We will analyze the distribution of the first harmonic x-component of the field strength, $E_{1,x}$, at distance $a/(2\pi)$ away from the collector, aiming at locating its extremes. The x-component of the field strength is defined as $E_x = -\partial\varphi/\partial x$. Therefore from ***Equations 1*** and ***2*** φ follows that

$$E_{1,x}(x,z) = \\ = A_1\frac{2\pi}{a}\exp\left(-\frac{2\pi z}{a}\right)\sin\frac{2\pi x}{a} \qquad (3)$$

Function $E_{1,x}$ has its extreme values at points $x = a/4$. Every odd extreme is a maximum and every even a minimum. Therefore at a point with coordinates $x = a/4$ and $z = a/(2\pi)$ the field strength component points to the left, while at point $x = 3a/4$ and $z = a/(2\pi)$ component $E_{1,x}$ points to the right side. This field distribution forces charged jet segments to form parallel strands bridging the space between neighbouring lamellae, since jet components are stretched horizontally and attracted to the neighbouring lamellae.

The field strength distribution around the special saw-like collector composed of lamellae was investigated numerically using the electrostatic application mode available in COMSOL Multiphysic. Computer simulation results are shown in detail in ***Figures 2.B*** and ***2.D***. The surrounding environment is considered as a square area that contains models of principal parts of the setup, particularly the spinning roll electrode and collector. The electrostatic potential value at the spinning electrode was +25 kV, while the collector was kept at -25 kV. The simulation was run with 14889 mesh points and 29056 elements including 720 boundary elements. The mesh elements were Lagrange – Quadratic and are presented in ***Figure 3***. The surrounding environment was modelled as air.

Results and discussion

Structure of nanofibrous materials

The cross section morphology of the yarn is depicted using a Zeiss ultra plus electron microscope, shown in ***Figure 4.A***. A detail view of the nanoyarn surface is depicted in ***Figure 4.B***. The photograph in ***Figure 4.C*** demonstrates the final yarn length - 50 cm. The diameter of nanoyarn varies from 0.7 to 1.2 mm. Its linear density, i.e., the fineness, is 1.3 cN/tex. The macro image obtained using the light microscope of the saw-like collector with nanofibrous mat is shown in ***Figure 4.D***.

The program NIS elements 3.0 was used for measuring fibre diameters. Nanofibre diameter data were collected from 100 measurements taken from SEM microphotographs similar to that in ***Figure 4.B***. The average value of these diameter measurements is 441.61 nm

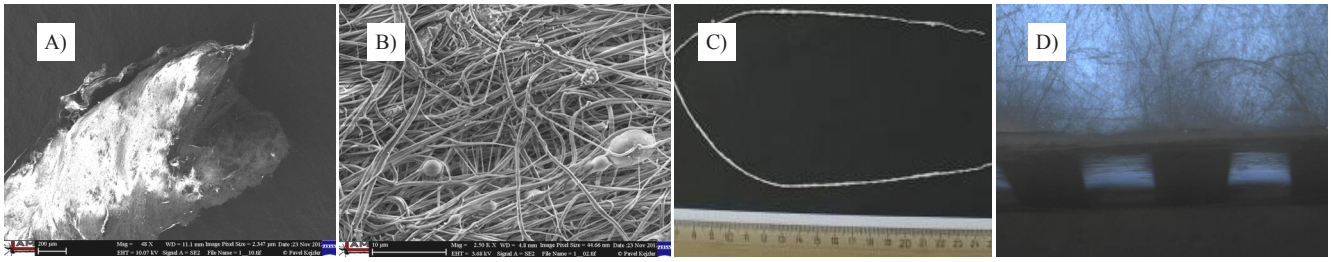

Figure 4. *(A) SEM picture of the cross section of PVA nanoyarn. (B) Detail view of surface of PVA yarn depicted using a Zeiss microscope. (C) Oriented nanofibrous material photograph of the PVA nanoyarn produced. (D) Detailed structure of the saw-like collector with deposited PVA layer, depicted using a macro scope.*

with standard deviation 143.93. These results show that the fibres are fine and relatively uniform. The deep frozen yarn was broken in liquid nitrogen. The liquid nitrogen caused the material to become fragile and break.

Conclusion

A simple method has been illustrated to prepare nanoyarns using the special saw-like collector. The electrostatic field in the vicinity of the collector enables to deposit parallel nanofibrous strands. Oriented strands were then twisted to form nanoyarns with a length of about 50 cm. Yarns were prepared from PVA polymer solution. The nanoyarns produced, consisting of nanofibres, can be used in various new applications including tissue engineering, forensic probes, linear materials for chromatography as well as for fabric and knitted textile compounds of nanoyarns.

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