Centrifugal spinning of nano-fiber webs - A parameter study of a novel spinning process

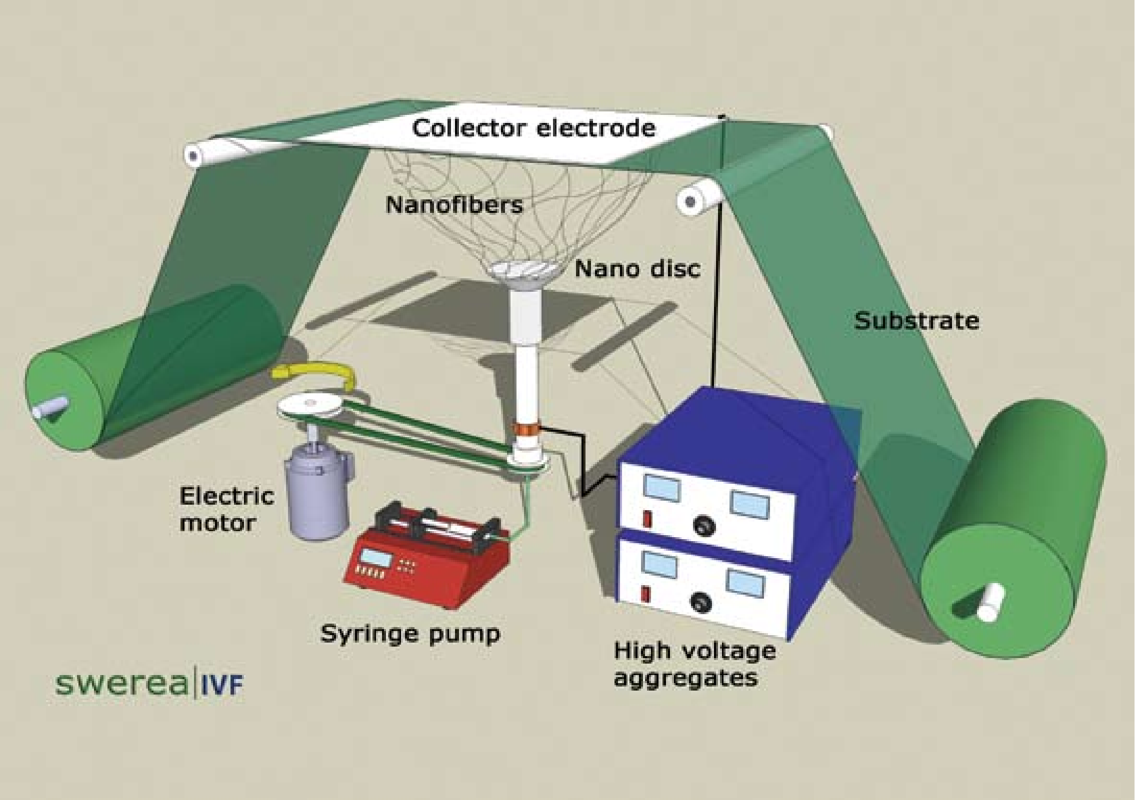

Figure 1. Device for nanofiber production.

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Introduction

A well known method of producing nanofibers is the electrospinning process. In this process[1,2] a polymer solution is subjected to electrostatic charging whereby the electrostatic repulsion overcomes the surface tension and results in the ejection of thin liquid jets. The jets are further stretched in an electric field under simultaneous evaporation of the solvent resulting in the deposition of a "nano-fibrous" non-woven fiber mat. Fibers can be produced from single or multiple capillary needles or by needlefree electrospinning from a free liquid surface[3]. By these processes fiber diameters well below 1 µm can be achieved. However, the production rate from the electrospinning process is low and scaled-up variants appear to be technically complex and expensive.

Recently, a novel device and process for large scale production of nanofibers was invented at Swerea IVF[4]. The process combines concepts of centrifugal spinning with electrospinning. The purpose of the present communication is to give a description of the new process and to present a phenomenological process parameter study. The main objective of the parameter study was to optimize the process parameters in order to obtain fibers thinner than 0.5 µm and with a minimum of defects in the nano-fibrous coating in the form of beads and holes. It is not within the scope to discuss in detail the physical background to the presented phenomena.

1. D. H. Reneker, I. Chun, *Nanotechnology*, 7(1996)216.
2. A. Frenot, I.S. Chronakis, *Current Opinion in Colloid and Interface Science*, 8(2003)64.
3. Tamara Van Kamp, Doctorial thesis, University of Gent, Belgium, 2009.
4. Swedish patent nr: 530751. Inventor: Bengt Hagström.

Novel fiber spinning device

The recently invented fiber spinning device is shown in Figure 1.

A detailed picture of the rotating disc is reproduced in Figure 2.

Figure 2. Rotating spinning disc manufactured from gold plated aluminum. Disc diameter is 100 mm.

A polymer solution is pumped and deposited centrally onto a quickly rotating spinning disc. Due to the centrifugal forces the polymer solution is transported radial towards the rim (perimeter) of the rotating disc where the surface tension is broken by the centrifugal force and a multitude of liquid jets are ejected. An electric field is applied between the disc and the collector electrode by a high voltage supply. The electric field is directing the liquid jets towards the collector and helps to stretch the jets to very fine dimensions under simultaneous evaporation of the solvent leaving a dry nano-fibrous coating on the substrate passing the collector plate. The total cost of the different components is less than 10.000 Euro and the construction can be made very simple and robust.

Process parameters and materials

The main objective of the parameter study was to optimize the process parameters in order to obtain fibers thinner than 0.5 µm and with a minimum of defects in the nano-fibrous coating in the form of beads and holes. The process parameters studied where 1) polymer concentration in solvent, 2) distance between disc and collector, 3) flow rate of polymer solution, 4) revolution speed of disc (rpm) and 5) electrical potential between disc and collector (voltage). The polymer was PA6 with M_n = 44000 g/mol (Ultramid 3300 from BASF). The solvent was formic acid. The substrate was a spun bond PET non-woven.

It should be noted that the process is insensitive to ambient conditions like temperature and humidity. This is a clear advantage compared to needlebased or needleless processes which sometimes produce very different results depending on relative humidity.

Defects

Two types of defects in the nano-fibrous coating deposited by the depicted spinning device have been identified to occur. These are beads and holes, as shown in Figure 3.

The beads vary in size from a few up to some 20-30 µm. They are formed by small polymer droplets. The formation mechanism is not known at the time being. Beads are considered less detrimental to many applications while the holes are certainly detrimental to applications like filter media, membranes and barriers. They are formed by larger drops that are still "wet" when reaching the substrate and there "melts" the already formed nanofibers.

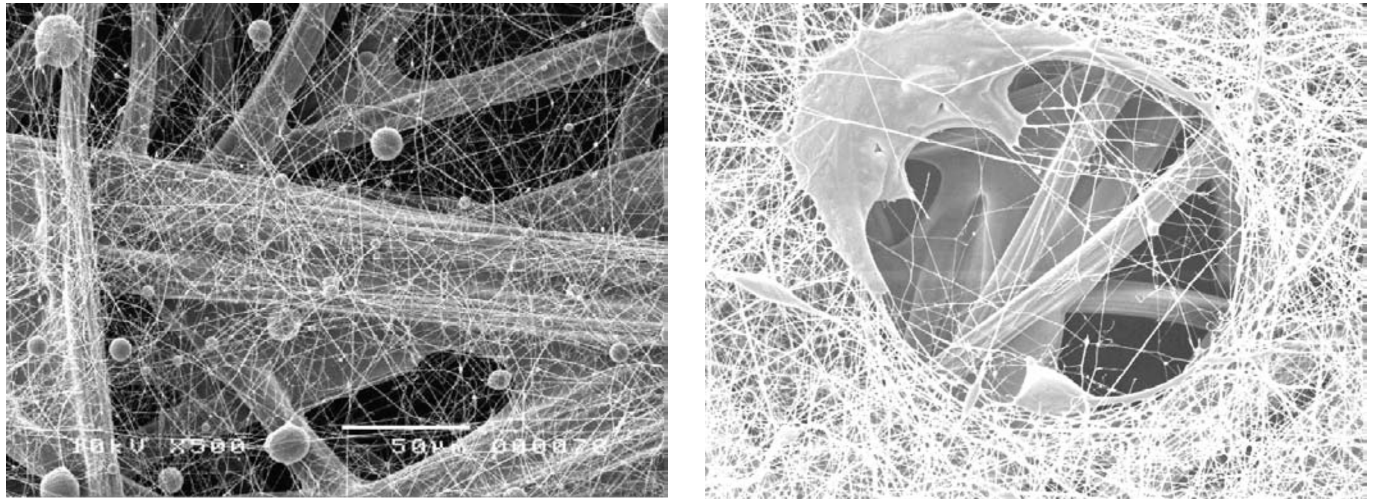

Figure 3. Defects in nanofiber coatings: beads (left) and holes (right). The background seen is the spun bond PET substrate.

Experimental design and evaluation

Factorial designed experiements

The worksheets for screening and full factorial investigation were achieved by the software MODDE[5]. To evaluate trends in the effect on fiber diameter and morphology for each of the five chosen process parameters, a screening was performed. Each parameter was given two levels, high and low, and center points were added as shown in Table 1.

Parameter	Low	High	Center
Concentration/ wt% PA6	10	16	13
Distance/ cm	36	56	46
Flow/ ml/min	4	8	6
Rotation/ rpm	2500	7500	5000
Voltage/ kV	50	100	75

Table 1. Parameter values for screening experiment

The fractional factorial design used in screening was acquired by a 2^{V-1} design resulting in 19 experimental runs. Samples were taken for each run and examined by scanning electron microscopy (SEM) and light microscope and an image analysis was performed to evaluate the response on average fiber diameter. Hole and bead occurrences were subjectively assessed for the different parameter settings. The discrete scale was in three steps: 1 = almost no beads or holes, 2 = some beads and holes, 3 = many beads and holes. After multiple regressions, hole and bead occurrences can adopt values in between these steps. These values are hard to interpret into real hole and bead occurrences. But a tendency is shown which can be used for minimization of holes and beads.

After the screening, three parameters were chosen as most important while rotation (6300 rpm) and voltage (100 kV) were held constant (Table 2). These were then investigated in a three level full factorial study, giving 27 runs, with an addition of 3 minimum points. Samples were taken for each run and examined by SEM and light microscope and an image analysis like the one performed during the screening was carried out.

Parameter	Low	Center	High
Concentration/ wt% PA6	7	10	13
Distance/cm	36	46	56
Flow/ml/min	4	6	8

Table 2. Parameter values for full factorial study

5 MKS Umetrics AB, Sweden

Results and discussion

Diameter distribution

The distribution of fiber diameters is rather broad. In Figure 3, a histogram with over 200 diameters measured from four different runs with the same parameter settings appears to have a normal distribution. The normal distribution (curve in the diagram) is $N(263,77^2)$ with the amplitude fitted to the histogram. A broad distribution of fiber diameters has also been found from needleless electrospinning from a free liquid surface[6]. Electrospinning from single capillary needles appear to produce more uniform fibers. The importance of this may vary with the application. The average diameter measured from SEM images was 263 nm in Figure 3. It should be noted that the actual diameter is somewhat lower since the fibers are sputtered with gold in order to avoid electrostatic charging by the electron beam in the SEM. The thickness of the gold layer can be estimated to be in the range 10-50 nm (20-100 nm on the diameter).

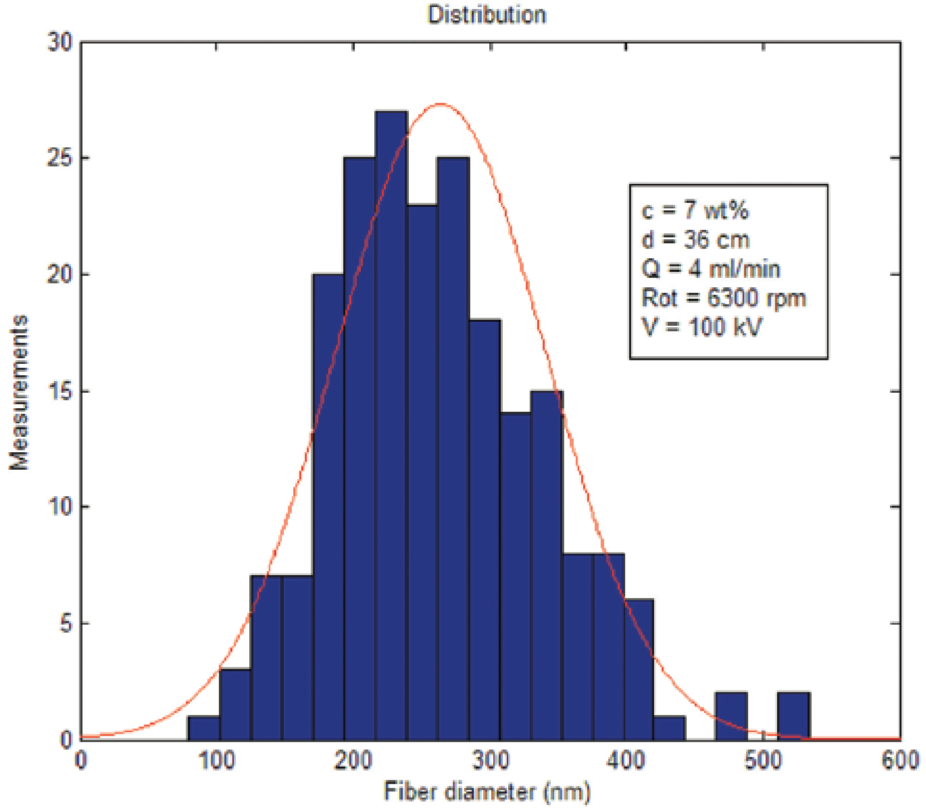

Figure 3. Diameter distribution for over 200 fibers showing a normal distribution

6. D. H. Reneker et al., *Nanotechnology*, 17(2006)1123.

Screening experiments

The parameter values for the screening experiment are shown in Table 1. The effect on fiber diameter, holes and beads for the different parameters is shown in Table 3. The overall confidence intervals for the main effects obtained from multiple linear regressions were wide for the fractional factorial study but the tendencies shown could be used to decide on which parameters to be used for a full factorial study.

Increasing parameter	Diameter	Holes	Beads
Polymer concentration	↑	↑	↓
Distance	↑	↓	↑
Flow rate	→	→	↑
Rotation speed	→	↓	↑
Voltage	↓	↑	↓

Table 3. Main effects of parameters in screening test.

It is seen that polymer concentration and electrical field strength (voltage divided by distance) are important for the resulting fiber diameter. Low concentration and high field strength promote thin fibers. This is intuitively what one would expect since a low concentration will reduce the viscosity and thus the resistance towards stretching of the liquid jet. An example of the effect of concentration on fiber diameter is shown in Figure 4.

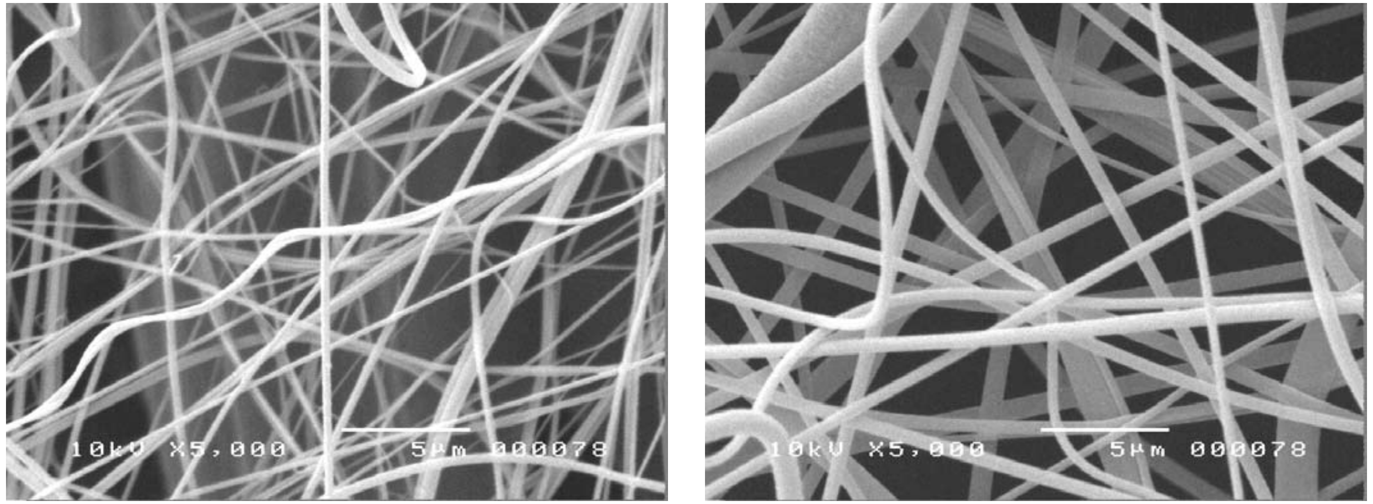

Figure 4. SEM-images (magnification was 5000x at 10 kV) from samples with 10 wt%, 2500 rpm (left) and 16 wt%, 7500 rpm (right). Distance, flow rate and voltage were held constant (d=36 cm, Q=4 ml/min, V=100 kV). The length of the scale bar is 5 µm.

Figure 4. SEM-images (magnification 5000x at 10 kV) from samples with 10 wt%, 2500 rpm (left) and 16 wt%, 7500 rpm (right). Distance, flow rate and voltage were held constant (d=36 cm, Q=4 ml/min, V=100 kV). The length of the scale bar is 5 µm.

High field strength will lead to a high charging of the jet and higher electrostatic force acting on the charges in the jet, both factors promoting stretching of the jet.

Flow rate and rotation speed has only little influence on fiber diameter. It seems fiber diameter is affected rather by parameters involving stretching of initiated fibers than by parameters affecting the flow of solution on the disc surface, as rotation speed and flow rate. Increasing the flow rate results in an increase in bead formation while no effect on hole occurrence is observed, which indicates that higher production rates can be achieved without affecting the number of holes. Since rotation speed had only little influence on fiber diameter it was held constant in the full factorial study.

Despite the fact that flow rate did not seem to affect fiber diameter it was kept as a parameter in the full factorial study since it will be crucial for production rates.

High viscosity seems to prevent bead formation. Beads are formed when surface tension is high comparing to viscosity and so the high viscosity at higher concentrations leads to less bead formation. This is unfortunate since thinner fibers are looked for in most applications, cf. filtration. At the same time more macroscopic holes are observed. These are probably formed from larger drops which have too small surface-to-volume ratio to solidify. Solvent is not vaporized and dissolve the fiber web when attracted to the substrate by the electric field. The concentration dependency on fiber diameter is of great interest in yielding thinner fibers and was therefore used as a variable in the full factorial study.

Full Factorial Study

The parameters chosen for the full factorial investigation were concentration, distance and flow rate, see Table 2. Since more information is gathered from full factorial investigations, smaller standard deviations are present giving narrower confidence intervals. The results are therefore more accurate and reliable than results from screening. The results are summarized in Table 4.
The full factorial study confirms the results from the screening, comparing Tables 3 and 4. Because of the strong dependence of fiber diameter on concentration, the concentration interval was switched to lower values; 7, 10 and 13 wt% of PA6 in formic acid, to gain even thinner fibers. Holes and beads were observed with the same dependencies as in the screening. For minimizing of fiber diameters, the concentration should be held as low as possible and with this decrease in concentration a decrease in holes is expected, which is a rather convenient coincidence. However, the beads are expected to increase in numbers and are the limiting factor for optimization by concentration manipulation.

Regarding distance, the fiber diameter and occurrence of holes is influenced in the same way as shown in the screening, but there is a difference in bead occurrence, compare Tables 3 and 4. The results from the full factorial study should be regarded as more accurate, but the measuring method is poor due to subjective estimations used for quantification. Shorter distances would then be preferable in minimization of fiber diameters (high field strength). A shorter distance, however, will also yield more holes, according to the used process interval, while the occurrence of beads is expected to be unaffected.

Increasing Parameter	Diameter	Holes	Beads
Concentration	↑	↑	↓
Distance	↑	↓	→
Flow rate	↓	→	↑

Table 4. Main effects of parameters in the full factorial test.

According to the screening, flow rate would have no effect on fiber diameter. The full factorial study, however, showed a small tendency of decreasing diameters with higher flow rates. Higher flow rates do not affect holes significantly, but more beads are to be expected. Outside the used interval other behaviors might occur, but scaling-up by increasing flow rate is probably possible without thickening of fibers or increasing of hole occurrence. To minimize fiber diameters and holes, the flow rate is to be as high as possible. This will, however, lead to substantial bead formation.

Production rate and fiber distribution

With the parameters used in the present study and a nanofiber surface weight of 1 g/m^2, the production rate reached was 30 m^2/hour. It is expected that further improvements of the process will facilitate production rates up to 100 m^2/hour from a single disc. By using multiple discs simultaneously, high production rates can be achieved. Due to the asymmetry of the disc compared to the substrate, the surface density of nanofibers is higher towards the edges of the substrate. For a 40 cm wide web, using a stationary spinning disc, the variation around the average surface weight was some ±20%. The uniformity can be improved by using multiple, reciprocating discs. The shape of the collector electrode may also be optimized for better uniformity.

Acknowledgement

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