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An investigation on quilled nozzle-less electrospinning in comparison with conventional methods for producing PAN nanofibers

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Abstract

Over the last decades by appearing nanotechnology electrospinning has been reconsidered as a significant method. However, electrospinning production rate is limited by the rate at which the polymer solution or melt is fed to a single jet. Feeding rate can be increased through implementing a wide range of methods such as multiple nozzle electrospinning. In the present work, an innovative "quilled" drum with a peculiar design was rotated in a PAN polymer solution in an electrical field to optimize energy consumption, uniform nanofiber distribution on the collector, and increase production rate. The produced nanofibers were compared with those produced from modified multi-nozzle and single-nozzle electrospinning methods. The mean diameters of nanofibers produced from the quilled drum was 32% greater than that of single-nozzle and 28% less than multi-nozzle electrospinning. The CV% of thickness of the webs were 7.9, 11.2, and 12.5% for the quilled, single nozzle and multi-nozzle methods, respectively which showed the presented method produced more uniform webs. The production rate of this electrospinning was 60 and 17 times more than single and multi-nozzle methods, respectively.

Keywords: Electrospinning, Nozzle-less, Nanofibers, Producing method

Introduction

Nanofibers are of great importance due to their high surface to volume ratio, porosity, and good mechanical performance in a wide variety of applications (Ciera 2011). They are used in vast areas such as tissue engineering (Semnani et al. 2017), wound dressing (Vargas et al. 2010), drug delivery systems (Hu et al. 2014; Zamani et al. 2010), filtration (Su et al. 2017), and self-cleaning surfaces (Huang et al. 2017). There are different methods for producing nanofibers such as drawing, template synthesis, phase separation, self-assembling, and electrospinning (Yoon et al. 2009; Zhang et al. 2005). In comparison with electrospinning, other methods can produce limited amount of nanofibers. In addition, these methods have more disadvantages. Drawing is a discrete method, self-assembling is complicated, phase separation is limited to special polymers, and template synthesis has fiber diameter limit (Caruso et al. 2001). On the other hand, electrospinning is widely used due to its cost effectiveness, simplicity, flexibility, and ability to use various range of polymers (Caruso et al. 2001; Hu et al. 2014; Ramakrishna 2005; Semnani et al. 2017).

Over the last decades by appearing nanotechnology electrospinning has been reconsidered as a significant method. However, electrospinning production rate is limited by the rate at which the polymer solution or melt is fed to a single jet (Li and Xia 2004; Theron et al. 2004). There are various methods to increase the production rate such as multiple nozzle electrospinning in which nanofibers with different polymer compositions can be produced (Theron et al. 2005). Nevertheless, utilizing multiple jets significantly increases the costs. Moreover, since the jet distribution is made artificially, the process has instabilities and the production of nanofiber layers is not homogenous (Petrik and Maly 2009). Another economical method to increase the production rate is nozzle-less electrospinning which can be used for nanofiber mass production (Rafiei et al. 2013). One of the most productive types of the above mentioned method is free liquid surface electrospinning in which the number and location of the jets are set up naturally in their optimal positions. (Petrik and Maly 2009).

Yarin et al. proposed a two-layer system in which the lower layer was a ferromagnetic suspension and the upper layer was a polymer solution. The layers were subjected to a normal magnetic field provided by a permanent magnet or a coil. Thus, multiple electrified jets were exposed to strong stretching by the electric field and bending instability. Finally, solvent evaporated and solidified nanofibers deposited on the upper counter-electrode, as in an ordinary electrospinning process. (Yarin and Zussman 2004).

Dosunmu et al. applied air pressure through the walls of a porous polyethylene tube to form multiple jets for electrospinning nylon 6 nanofibers from a 20 wt% solution. The fibers had a similar mean diameter to those produced from a single nozzle method in spite of broader distribution. Their mass production rate was 250 times greater than that of a typical single nozzle method (Dosunmu et al. 2006).

Varbhas et al. also used a tube having a porous wall to electrospin polyvinylpyrrolidone (PVP) from a polymer solution of 15 wt% by the help of low air pressure of 1–2 kPa through the tube wall. They used an electric field of 40–60 kV. They showed that from a 13 cm long tube with 20 holes, 0.3–0.5 g/h of nanofiber could be produced (Varabhas et al. 2008).

Lukas et al. observed, analyzed, and compared jetting from free liquid surface on specially designed linear cleft electrospinner with the theoretical predictions and obtained satisfactory results (Lukas et al. 2008).

Shin et al. used a simple unique needleless method. They employed charged vertically oriented threaded rods for holding multiple drops to launch many simultaneous jets. They conducted their tests with a single or multiple rods arranged in a linear array. They showed a single rod of about 50 cm in length could produce PVP fibers at a rate of 4.5 g/h and 200–400 nm size range (Shin et al. 2015).

Holopainen et al. developed a needleless electrospinning setup named "Needleless Twisted Wire Electrospinning". They used PVP, hydroxyapatite (HA) and bioglass to electrospin nanofibers from a surface of a twisted wire set to a high voltage. Their production rates for PVP and HA were 5.23 and 1.40 g/h, respectively (Holopainen et al. 2014).

In this work, a method of electrospinning is presented to optimize energy consumption and uniform nanofiber distribution on the collector which leads to more even thickness of the derived mat through the width. Thus, an innovative "quilled" drum with a peculiar design was rotated in a polymer solution in an electrical field. The produced nanofibers were compared with those produced from multi-nozzle and single-nozzle electrospinning methods.

Methods

Materials

An 11 wt% solution of Polyacrylonitrile (PAN, Sigma Aldrich, MW: 150,000 Da, the US) was prepared by dissolving PAN in *N*, *N*-dimethylfomamide (DMF, Merck, Germany) for 24 h in an ambient temperature of 25 °C on a magnetic stirrer.

Electrospinning set up

Three different electrospinning setups were used in the present work. Setup A, was the ordinary single-nozzle electrospinning with a syringe with a needle gauge of 23. In setup B, 3 identical syringes with the same needle gauge number with setup A, containing identical polymer solutions, were arranged in a 1×3 matrix with an inter-nozzle distance of 25 mm. All jets in the above mentioned setups were subjected to the same voltage of 15 kV and polymer solution feeding rate of 0.28 ml/h. The collector for both methods had an rpm of 50. A high voltage–power supply (Fanavaran Nano-Meghyas, HV35P OV, Iran) was used to control the voltage. A syringe pump (Fanavaran Nano-Meghyas, SP1000, Iran) was used for polymer solution feeding. Schematic diagrams of single and multi-nozzle electrospinning and a typical laboratory single-nozzle electrospinning as an example are shown in Figs. 1 and 2, respectively.

In setup C, as shown in Fig. 3, a "quilled" drum with an external diameter of 80 mm and a rotating speed of 5 rpm was floated in the polymer solution. The collector drum rotated with an rpm of 50. The "quills" were pinned in 8 rows on the periphery of a smooth cylinder with a diameter of 60 mm and length of 160 mm. The rows were formed

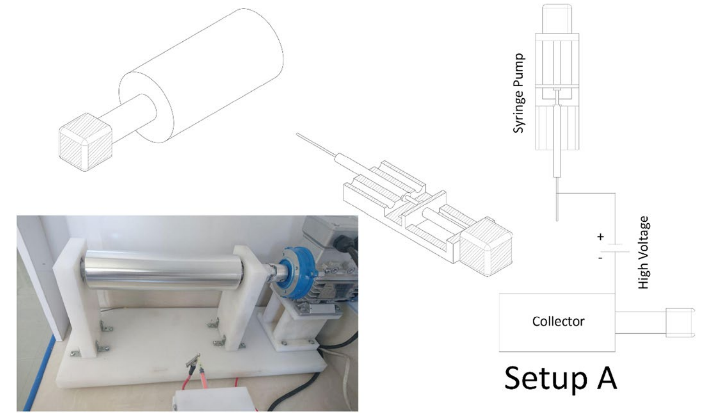

Fig. 1 Single-nozzle electrospinning setup

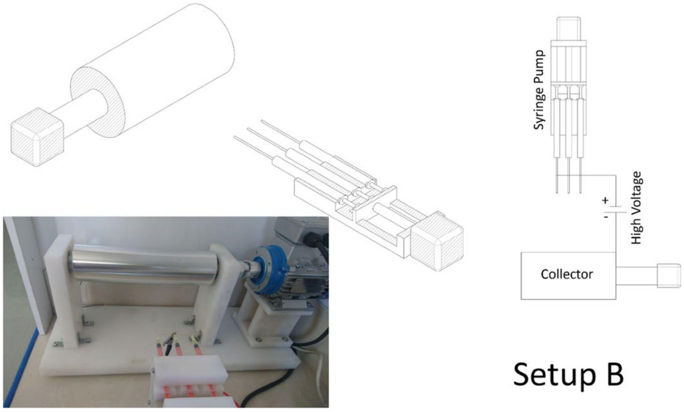

Fig. 2 Multi-nozzle electrospinning setup

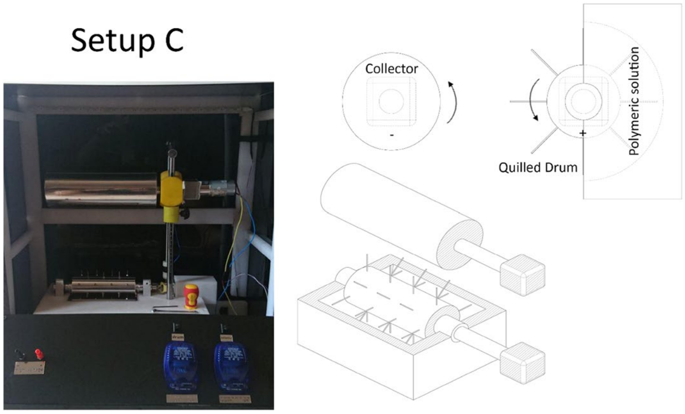

Fig. 3 Quilled nozzle-less electrospinning setup

Table 1 Electrospinning parameters

Electrospinning type	Voltage (kV)	Distance to collector (cm)	Feeding ratio (ml/h)
Single nozzle	15	15	0.5
Multi-nozzle	15	15	0.5 × 3
Quilled nozzle-less	25	10	–

with the same distance from each other. Each quill had a distance of 40 mm from the adjacent one in the same row and was placed between two quills in the adjacent rows. The quills of every other row were located in a 20 mm margin from the edges of the drum while the quills in the adjacent rows had a margin of 40 mm. Thus, 4 rows had 4 quills and 4 rows had 3. Jets were formed on the apex of the quills and PAN was electrospun. Table 1 gives the parameters for electrospinning PAN solution in three different methods.

As it can be seen from Table 1, the voltage and jet distance to collector in setup C are different from the other two setups. The number of jet positions for fiber formation in setup C was greater than the other two methods. Therefore, the electrical potential had to be increased by increasing the voltage and decreasing the jet to collector distance.

PAN nanofibrous mat samples were then taken for scanning electron microscopy (SEM, Philips X130, Netherlands). After that, the thicknesses of the webs were measured using a digital thickness gauge (BAER 674, Switzerland). Next, diameters of 100 fibers in each web were measured by Digimizer software and nanofibers mean diameter and diameter histogram were reported.

Results and discussion

Figure 4 shows diameter distribution and SEM images of electrospun PAN nanofibers and Table 2 reports their mean diameter and production rate in the three setups. The mean diameters of nanofibers produced from setups B and C were 84 and 32% greater than that of setup A, respectively.

The production rate of the presented method was drastically greater than those of setups A and B. In this method, in the optimum rpm of 5 and according to the special arrangement of the quills, there was a potential of forming 28 jets in each rotation. The jets were formed naturally on the apex of the quills and thus the optimized paths were selected by

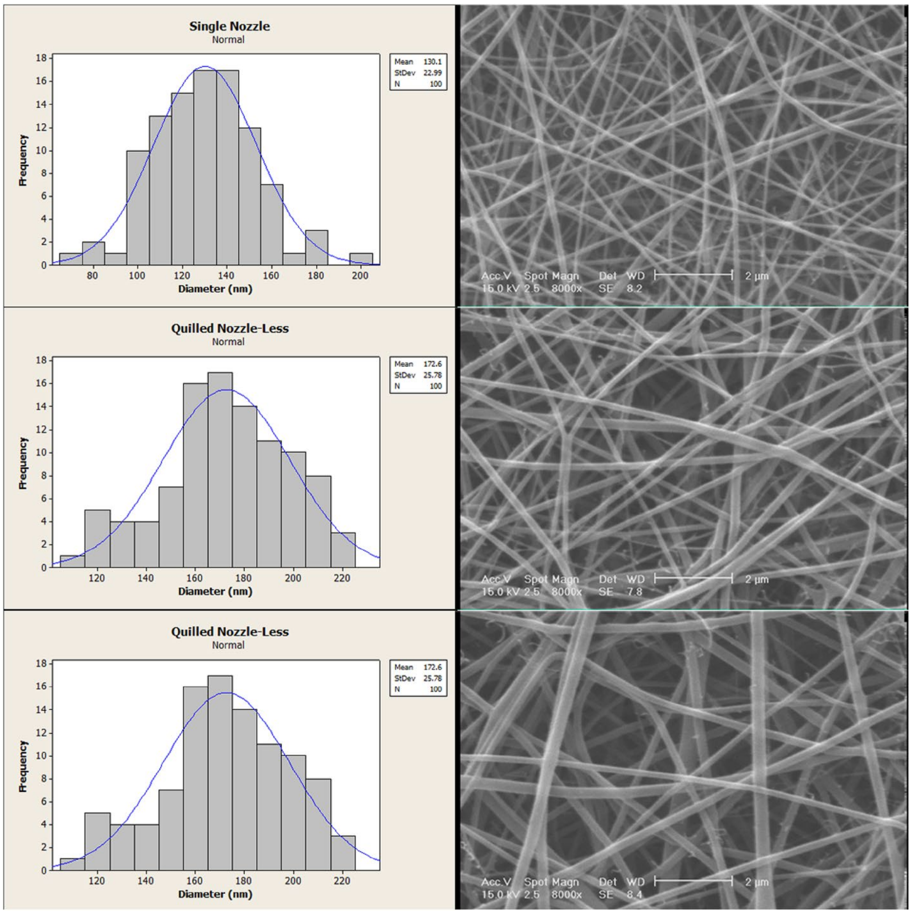

Fig. 4 SEM images of electrospun and diameter distribution of PAN nanofibers produced in three different methods

Table 2 Mean diameter and production rate of various electrospinning setup

Electrospinning type	Mean diameter (nm)	Standard deviation of diameter	Production rate (gr/h)
Single nozzle	130	22.99	0.12
Multi-nozzle	239	34.22	0.43
Quilled nozzle-less	171	24.56	7.2

Table 3 Thickness of PAN nanofibers mats

Electrospinning type	Thickness (μm)	Standard deviation	CV%
Single nozzle	35	3.94	11.2
Multi-nozzle	46	6.72	12.5
Quilled nozzle-less	79	6.47	7.9

them. Therefore, the jets were free to be deposited from the randomly determined positions to the collector drum and the production rate was increased. Moreover, in this method all the jets can be supplied by a single power supply with less voltage in comparison with other methods due to the absence of syringe pump and consequently the simplicity of jet forming.

Table 3 reports the thickness in 30 different randomly selected points of the electrospun webs. It should be noted that the weights of the webs were normalized based on time. Thus, for evaluating webs uniformity the thickness of each nanofibrous web produced in different time was measured. The thickness of PAN web in setup C was more uniform in comparison with setups A and B.

In a multiple-nozzle electrospinning, in addition to the external electric field and self-induced coulombic interactions which influence the jet path, mutual-coulombic interactions between different jets are also effective (Theron et al. 2005). Thus, a decrease in the distance between every two nozzles results in greater repulsion between the jets. In addition, decreasing the inter-nozzle distance leads the onset of the electrically driven bending instability, which is the main factor for reducing the fiber diameter to the nanometer scale, to delay. For compensating this delay, the distance between needle and collector should be increased (Theron et al. 2005). However, the distance between the collector and the needle is limited, the above mentioned delay can be requited by increasing the inter-needle distance.

In the present work, the quills were arranged in a way that in each rotation only one row of the quills were responsible for generating jets. Thus, there was no perturbation between the electric field of each row. Moreover, each quill was 40 mm away from the adjacent one and hence the interactions between the jets were reduced. On the other hand, the arrangement of the quills was in a way that each one could deposit polymer solution to the collector drum in even distances which led to a more uniform web formation as appose to multi-nozzle method. Unlike the stripes which were formed in the latter method, in the presented electrospinning no stripes were observed.

Conclusion

In the present work a new method of electrospinning was introduced by floating a quilled drum in PAN solution. The production rate of the presented method was drastically greater than those of single and multiple-nozzle methods. The quills were arranged in a way that in each rotation only one row of the quills were responsible for generating jets. Thus, there was no perturbation between the electric field of each row. Moreover, the interactions between the jets were reduced by imposing a sufficient distance between them. Having the potential of forming 28 jets on the apex of the quills in each rotation, the jets were free to be deposited from the randomly determined positions to the collector drum and the production rate was increased. The arrangement of the quills was in a way that each one could deposit polymer solution to the collector drum in even distances which led to a more uniform web formation as appose to multi-nozzle method.

Authors' contributions

MA and MH designed the quilled nozzle-less electrospinning setup and carried out the experiments and rounded up data. MH and SPRT developed the literature review. DS suprvised the whole process. SPRT and MH guided the analysis of the results and conclusions and contributed to the formatting and editing of the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Not applicable.

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