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3D printed multiplexed electrospinning sources for large-scale production of aligned nanofiber mats with small diameter spread

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Abstract

We report the design, fabrication, and characterization of novel, low-cost, and modular miniaturized nanofiber electrospinning sources for the scalable production of non-woven aligned nanofiber mats with low diameter variation. The devices are monolithic arrays of electrospinning emitters made via stereolithography; the emitters are arranged so each element has an independent line of sight to a rotating collector surface. Linear and zigzag emitter packing were evaluated using a PEO solution with the aim of maximizing the throughput of nanofibers with the smallest diameter and narrowest distribution. Current versus flowrate characterization of the devices showed that for a given flowrate a zigzag array produces more current per emitter than a linear array of the same emitter pitch and array size. In addition, the data demonstrate that larger and denser arrays have a net gain in flow rate per unit of active length. Visual inspection of the devices suggests uniform operation in devices with as many as 17 emitters with 300 μm inner diameter and 1.5 mm emitter gap. Well-aligned nanofiber mats were collected on a rotating drum and characterized; the 17-emitter device produced the same narrow nanofiber distribution (∼81 nm average diameter, ∼17 nm standard deviation) for all tested flow rates, which is strikingly different to the performance shown by 1-emitter sources where the average fiber diameter significantly increased and the statistics notably widened when the flowrate increases. Therefore, the data demonstrate that massively multiplexing the emitters is a viable approach to greatly increase the throughput of non-woven aligned nanofiber mats without sacrificing the statistics of the nanofibers generated. The production of dry nanofibers by the 17-emitter array is estimated at 33.0 mg min\textsuperscript{-1} (1.38 mg min\textsuperscript{-1} per mm of active length), which compares favorably with the reported multiplexed electrospinning arrays with emitters distributed along a line.

Keywords: 3D printing, electrospinning, high-throughput nanomanufacturing, multiplexed electrospray sources, nanofibers

(Some figures may appear in colour only in the online journal)

1. Introduction

Electrospinning is a physical process in which ultrathin fibers are generated via electrohydrodynamic jetting. The feedstock is usually composed of long-chain polymers dissolved in a polar solvent, whereby the solvent evaporates during the
spinning process while the jet generated travels from the electrospinning emitter to a collector [1]. The jet is mainly subject to two forces with opposing effects [2], i.e., (i) electrostatic repulsion of the charges in the jet that decreases the fiber diameter, and (ii) surface tension pulling that tries to break up the jet into droplets. If the viscosity of the liquid is high enough and the fluid contains long-chain molecules the electrostatic repulsion prevails, resulting in a jet with very small diameter that becomes a filament after drying. The fiber morphology is controlled by parameters such as the applied electric field, the distance between the emitter and the collecting substrate, temperature, flow rate, humidity, and properties of the feedstock including the dissolved, concentration, surface tension, conductivity, and viscosity [3]; in general, these parameters are interrelated.

Non-woven aligned nanofiber mats are of great interest in applications that exploit the arrangement of the fibers, e.g., directionally reinforced nanocomposites with enhanced mechanical or thermal properties, biomedical applications where cell proliferation is improved by the aligned layering of the fibers. In particular, biomedical devices such as tissue engineering scaffolds, drug release devices, and biochemical sensors require a biocompatible surface material such as polyactic acid [4], polyethylene oxide (PEO) [5, 6], polyvinyl alcohol (PVA) [7, 8], chitosan [9, 10], chitosan with PEO [11–15], polyactic-co-glycolic acid-chitosan with PVA [16], and chitosan with PVA [17] to achieve cell proliferation. Electrospun nanofibers can be collected into non-woven mats with fibers layered aligned using structured electrode collectors [18] or a rotating surface [19]. In the latter approach, several collector designs including drum, wire drum, and disc collectors [20] have been adapted to produce nanofibers in various biomaterials, e.g., PVA and PEO [21, 22]. A rotating drum aligns nanofibers based on the tangential speed of the collector surface; when the surface speed is smaller than the alignment speed, the fibers are deposited randomly [23]. However, fiber breakage may occur if the rotating speed is excessively high [24].

Manufacturing unwoven nanofiber mats at a high production rate remains a challenge. Some efforts have focused on modifying the collector design [24], expanding the number of emitters [20, 25–32], and increasing the flow rate [33]; nonetheless, multi-emitter designs have proven more effective than increasing the flow rate [28]. The multi-nozzle electrospinning sources reported in the literature can be classified by the way of supplying the feedstock: there are systems with spouts fed individually through syringes [25–27, 29, 32], and multi-nozzle systems where the feedstock is driven from a common reservoir to each nozzle [28, 31]. The maximum emitter density in a multiplexed electrospinning source is influenced by the emitter pitch and the emitter geometry. For example, Varesano et al [27] described an array of up to nine emitters with 2 cm emitter pitch distributed in two columns. In contrast, Yamashita et al [28] and Tomaszewski et al [31] reported a minimum gap between emitters of 3 mm; a smaller spacing caused merging of the jets from adjacent emitters into droplets.

Microfabricated multiplexed electrospinning sources have also been explored to increase nanofiber throughput [34]. Microfabrication technology can circumvent some of the manufacturing challenges faced by these systems including the tight control of the dimensions, the monolithic creation of the emitter arrays with the feedstock supply network, and the miniaturization of the emitters to achieve larger emitter density and operation at less bias voltage. In particular, Ponce de Leon et al reported a planar electrospinning emitter array made of silicon via deep reactive-ion etching with 225 emitters spaced 2 mm [35].

Additive manufacturing, i.e., the layer-by-layer construction of devices using a computer-aided design (CAD) file [36], has been recently explored as a manufacturing toolbox for micro-systems. Researchers have shown 3D printed devices with performance on par or better than counterparts made with standard microfabrication [37, 38], and also demonstrated designs not previously attainable due to fabrication complexity [39, 40]. In addition, the manufacturing time and cost of a complex 3D printed microfluidic system are significantly less than those incurred in traditional microfabrication, making possible to iterate multiple times the design and to satisfy a wider range of commercial applications.

This work reports novel 3D printed multiplexed electrospinning sources for scalable production of aligned nanofibers with low diameter distribution using a rotating drum as collector. The devices were made via digital light processing-stereolithography (DLP-SLA), which is an additive manufacturing technology that creates solid objects by photopolymerization of a liquid resin [36]. DLP-SLA can create freeform objects with cavities at high resolution. The 3D printed devices were characterized using a PEO solution as feedstock. Per-emitter current versus emitter flowrate data were acquired for devices with different emitter packing, emitter density, and array size, looking to maximize the flow rate per axial length of collector. In addition, metrology was conducted on non-woven aligned nanofiber mats created using different devices and emitter flow rates in a home-built rotating drum apparatus to determine the conditions for high-throughput generation of thin, uniform fibers.

2. Methods and materials

2.1. Feedstock

PEO (Mw = 900 000) and deionized water (DI) were purchased from Sigma-Aldrich (Sigma-Aldrich, USA). PEO fibers were spun from 4 wt% PEO in DI water; the PEO solution was created by adding PEO to the DI water while stirring at 80 °C for 3 h; the solution was cooled down and conserved at room temperature overnight before being used. According to Jin et al a 4 wt% PEO solution in DI water at the same molecular weight has a viscosity of ∼1.25 Pa s at a shear rate of ∼100 s⁻¹ [41].

The use of PEO in this study is motivated by its biocompatibility [42] and remarkable performance for cell proliferation in nanofiber membranes [43]. Fong et al investigated the properties of PEO solutions for electrospinning, establishing
that higher viscosity and a reduced surface tension favor the formation of fibers without beads [44].

2.2. Device design

The devices used in this study have the emitters spatially arranged so that each element has an independent line of sight to a rotating drum or a roll-to-roll manufacturing setup. Two packing configurations were explored: in the linear arrays the emitters are distributed along a straight line, while in the zigzag arrays the emitters are distributed along a line twisting around a straight line. For the same emitter pitch the zigzag devices (figure 1(a)) have half the projected emitter pitch (i.e., emitter gap) of the linear arrays (figure 1(b)); therefore, a zigzag array has twice the emitters per unit of length of a linear array with the same emitter pitch. This is significant because the closer the emitters are, the weaker the electric field acting on the emitter tips is, which decreases the current produced per emitter and even inhibits emission. Zigzag arrays of 3, 7, 9, 11, 13, 17, 21, and 25 emitters and linear arrays of 1, 7, and 9 emitters were manufactured; in each array, the maximum distance between the outermost emitters is equal or smaller than 24 mm, and the emitter gap varied between 12 mm and 1 mm.

The 3D printed multiplexed electrospinning sources have a rectangular body with a length of 38.67 mm, a width of 24.25 mm, and a height of 15.25 mm (measured from the central inlet to the spouts). The design consists of a 1.56 mm diameter central inlet (figure 1(c)) that supplies the feedstock into an internal tank with a total height of 3 mm a length of 31.25 mm and a width of 12 mm. The feedstock tank is internally reinforced by an array of 1.5 mm wide square columns to provide support to the ceiling of the 3D printed structure; the columns have a 500 μm radius fillet on both ends for a smooth liquid distribution. A horizontal 900 μm wide microfluidic channel in zigzag is embedded into the ceiling of the tank and serves as manifold to distribute the feedstock to a series of vertical feed meandering coils; each coil delivers feedstock to a different emitter and acts as a hydraulic impedance that ballasts the emitter. The coils are uniformly tapered, with an inlet diameter of 900 μm, decreasing to 700 μm at the outlet. The shape of the coils maximizes the emitter density and minimizes the device volume (in a planar array, the feed coils would be helical as in [39]). Each emitter has a 4 mm-tall conical body with a diameter at the base equal to 1.9 mm and a diameter at the top (spouts) equal to 1.6 mm; the geometry of the emitter eliminates in many cases the merging of the jets (see section 4). Each emitter has a vertical tapered channel at the center with an inlet diameter equal to 700 μm and a diameter at the spout equal to 300 μm, which is the minimum feature size of the multiplexed electrospinning source proposed in this study. The tapered hydraulics makes the filling-in pressure lower than the dripping pressure (i.e., the pressure needed to break the menisci at the emitter spouts), facilitating the supply of feedstock to all the emitters before activation.

2.3. Device manufacturing

The devices were made with the low-cost (<$3500), high-resolution DLP-SLA 3D printer Solus and the resin Solu-sProto (Junction 3D, Santa Clarita, CA, USA); the printer uses a modified commercial DLP projector as UV source. Each design was first created as a parametric model using the commercial software SolidWorks 2015 (DS SolidWorks Corporation, Waltham, MA, USA); the model was then
converted to a 3D mesh file in STL format with a resolution of 2 μm, i.e., an order of magnitude smaller than the pixels of the 3D printer. After that, the file is processed by the software Contour (Junction 3D, Santa Clarita, CA, USA), transforming the 3D mesh into 25 μm tall slices that are communicated to the printer and the projector. The printer creates, layer by layer, the solid object by polymerizing the resin at the bottom of the vat with UV light patterned by the projector; the printed object is attached to a build platform that moves back and forth within the vat, replenishing the resin at the bottom of the vat and correcting the amplitude of the movement as the printing job progresses. After the printing process is completed, the device is detached from the platform using pliers in twisting motion to avoid scratching the surface of the platform. The cleaning process consists in immersing the device twice in isopropyl alcohol (IPA) for 5 min, replacing the bath in between. A bottle with a dispensing needle is connected to the inlet of the device and IPA is pressure fed, removing the uncured resin from the channels; unlike most SLA resins that are gooey, the resin SolusProto has water-like viscosity, which greatly facilitates the cleaning operation. The channels are blown using compressed dry air (CDA) fed to the inlet of the device, and the IPA/air channel purge operation is repeated until visually confirming that no more uncured resin is coming out of the device and that all the emitters are ejecting uniformly IPA when the inlet of the device is fed with a dispensing needle. Finally, the devices are dried with CDA and put in a UV curing chamber (XYZ printing, San Diego, CA, USA) for 10 min.

Previously to print the electrospinning sources, resolution matrices were printed and measured to assess the capabilities of the printer and the resin (figure 2). The resolution matrices were plates with arrays of vertical cylinders spanning a range of diameters and heights; the diameters of the cylinders were varied between 75 and 1400 μm in multiples of the printer pixels (25 μm), while the heights of the cylinders were varied between 100 and 2000 μm in multiples of the slicing height (also 25 μm). Cylinders with diameters larger or equal to 200 μm were measured using a Mitutoyo Quick Vision ACTIVE 202 optical microscope with a 1.5X objective lens and 100 nm resolution, while the cylinders with diameters smaller than 200 μm were measured with a Leica Microsystems’ research-grade microscope incorporated with the Renishaw Invia Reflex Raman Confocal Microscope system equipped with a motorized stage for area mapping with in-plane step sizes of 100 nm and vertical step size of 16 nm. For each combination of diameter and height, 35 nominally identical cylinders were measured. The metrology shows close correspondence between the dimensions of the CAD models and the printed objects. The printed heights of the cylinders are about 0.6% larger than the CAD file and have an offset of 16 μm (about one slice), while the printed diameters are about 1.7% larger than the CAD file and have an offset of 7 μm (smaller than a pixel). The average standard deviation of the in-plane and out-of-plane features is 7 μm and 0.5 μm, respectively.

Figure 3 shows a 3D printed 17-emitter electrospinning source with zigzag emitter packing; figure 3(a) is an isometric view of the device next to a one-cent US coin as comparison, figure 3(b) is a top view of the device with a close-up view of a cluster of emitters, and figure 3(c) is the lateral view of the device. The volume of the device is 6.95 cm³, costs ~$2 in printable material, and takes ~60 min to print.

3. Experimental setup

3.1. Emitted current versus flow rate characterization

Figure 4(a) is a schematic of the experimental setup used to collect current versus flow rate characteristics from the 3D printed devices. The apparatus supplies feedstock to the device, biases voltages to the device and to a collector electrode, measures the current emitted by the device, and allows for fine adjusting of the separation between the emitter spouts.
and the collector electrode. In the setup, the miniaturized multiplexed electrospinning source is clamped to an aluminum chuck using M4 nylon screws; the top surface of the chuck has a groove with an O-ring that surrounds an orifice; when clamped, the bottom of the device squeezes the O-ring to make a watertight connection between the inlet of the device and the liquid feed. The chuck is secured to a vertical translation stage VAP10 (Thorlabs, Newton, NJ, USA) using a polypropylene sheet mounted on an aluminum breadboard fixed with 90° mounting adapters. The vertical stage is attached on an aluminum base plate protected with polypropylene sheets to insulate the fixture. The distance between the collector electrode and the emitter spouts is controlled using a fine adjustment knob with a resolution of 1.27 mm per revolution. A syringe pump NE-1000 (New Era Pump Systems Inc., Farmingdale, NY, USA) supplies PEO solution at different flow rates through a central flangeless nut made of PFA resin (IDEX Health & Science LLC, Oak Harbor, WA, USA), which was screwed to the back of the aluminum chuck. The aluminum chuck is electrically grounded.

A 4 inch wide stainless-steel square electrode positioned 8 cm away from the emitter spouts was covered with an aluminum foil sheet to collect the nanofibers. A bias voltage of −20 kV with respect to the aluminum chuck was applied to the collector electrode using a dual output high-voltage power supply (Gamma High Voltage, Ormond Beach, FL, USA). The current emitted by the device was measured using a picoammeter 485 Keithley (Tektronix, Cleveland, OH, USA) and data signals were recorded using an oscilloscope DS6104 (Rigol, Beaverton, OR, USA). Also, an external 5 MΩ high-voltage resistor (Newark, Chicago, IL, USA) was used to protect the picoammeter in the event of an electric short.

In a typical experiment the device was first tested dry to verify electrical insulation between the device and the collector electrode; an average leakage current of 0.77 nA was measured, which is over two orders of magnitude smaller than any of the currents measured in the wet experiments. The devices were then fed with PEO solution at a given flow rate and the total current was measured after visually confirming that a Taylor cone on each spout was formed; the current was very stable during the acquisition time. The flow rate was varied and a new current measurement was conducted, until a given flow rate range was covered. The per-emitter current and per-emitter flow rate were estimated by dividing the corresponding quantities by the number of emitters of the device. The experiments were monitored with a 5 MP CCD color digital camera attached to a 12X zoom microscope lens. After running experiments, the device was flushed with DI water to remove any leftover feedstock within the device; finally, the device was dried with CDA and stored for future reuse.

3.2. Aligned nanofiber collection and metrology

After current versus flow rate characterization, selected 3D printed devices were used to generate non-woven aligned nanofiber mats using the apparatus shown in figure 4(b). In the setup, the 3D printed electrospinning source is secured to the aluminum chuck described in section 3.1. Also, the PEO solution was supplied by the syringe pump to the device while a bias voltage of 20 kV with respect to the collector electrode was applied to the chuck using a dual output high-voltage power supply. The collector electrode is a rotating drum that is grounded, i.e., the polarity and magnitude of the bias voltage in the aligned nanofiber collection experiments are identical to those of the current versus flow rate experiments.
The emitters are aligned with respect to the axis of the drum, and the separation between the emitter spouts and the edge of the drum was set at 8 cm (i.e., the separation used in the current versus flow rate characterization).

The rotating drum collector subsystem consists of a 4 inch diameter aluminum cylinder mounted on electrically insulated bearings that are secured to a 0.75 inch thick chemical-wear resistant sheet by using nylon screws and PTFE washers; the drum is rotated by a DC motor with a controller (McMaster-Carr, Robbinsville, NJ, USA). A 6 inch wide and 0.125-in thick horizontal polyethylene plate was positioned at the drum height to prevent the generation of an air cushion around the collector surface that inhibits the collection of the nanofiber mats. The chuck and rotating drum subsystem are enclosed in a desiccator with pressure-controlled nitrogen flow feed (Terra Universal Inc., Fullerton CA, USA) to control the relative humidity during the collection of the nanofiber mats. A temperature and relative humidity sensor EasyLog data logger (Dataq Instruments Inc., Akron, OH, USA) was installed inside the chamber to monitor the relative humidity and temperature during the experiments. Preliminary studies were conducted to define the optimal nitrogen flow pressure and relative humidity for depositing the nanofibers, resulting in 20 psi nitrogen pressure and 20% relative humidity, respectively.

Preliminary studies were conducted to select the collector surface material; a repeatable collection of aligned nanofibers was achieved directly on the aluminum drum surface. The nanofiber mats were carefully retrieved from the surface of the drum and placed on a SEM pin stub mount, to then be coated with a 10 nm thick carbon coating using a Q150T Turbo-Pumped Sputter Coater (Quorum Technologies, Sacramento, CA, USA). Afterward, samples were measured with a Merlin Carl Zeiss SEM (Zeiss, Germany) with a 3 kV accelerating voltage. For each device tested, aligned nanofiber mats were collected for different flow rates. For each flow rate, metrology of 100 diameter fiber measurements was performed to obtain fiber size distributions. Fiber diameters were measured by ImageJ software (National Institute of Health, Bethesda, MD, USA) drawing parallel lines along the edges of the fibers and measuring the distance between the lines. The histograms were calculated using categories from 20 to 25 nm and around 5–9 bin sizes across the distribution.

4. Experimental results and discussion

4.1. Per-emitter current versus flow rate characteristics

Table 1 summarizes the geometry specifications of the different zigzag and linear devices tested with the maximum flow rate per emitter, per device, and per device’s active length (i.e., 24 mm, which is the useful length of the internal feedstock tank; the active length is what would be tiled in a longer device) that was achieved on each device while operating uniformly (figure 5). The data suggest that there is a trend of achieving smaller maximum per-emitter flow rates in devices with smaller emitter gap; however, the device with the largest flow rate and flow rate per unit of active length correspond to the largest array size with the smallest emitter gap. In other words, a device with larger emitter gap increases the maximum flow rate that can be sprayed by each emitter, while a device with larger array size increases the total flow ejected by the device, with a net gain in total flow rate for larger/denser arrays. For a given device, feeding a larger emitter flow rate than the quoted maximum caused dripping, which eventually led to jet merging and non-uniform jet operation. In all cases, 1 ml h⁻¹ was the minimum per-emitter
flow rate that resulted in the stable generation of a jet from each emitter.

It was not possible to activate simultaneously all emitters of the zigzag arrays with 21 (2.4 mm emitter pitch) or 25 emitters (2 mm emitter pitch) at any flow rate without having the jets merging or dripping, or having intermittent operation of the emitters; we hypothesize that the small emitter pitch made the electric field acting on the emitter tips too low for the formation of a stable jet per emitter. Although Liu et al reported formation of multiple jets from an emitter between dripping events [45], such fiber generation mechanism is less attractive because it does not efficiently use the feedstock. The intermittent emitter operation was also observed by Tomasweski et al in arrays of emitters with small emitter separation [31].

Table 1. Summary of specifications of tested 3D printed multiplexed electrospun nanofiber sources.

<table>
<thead>
<tr>
<th>Array packing</th>
<th>Array size</th>
<th>Emitter pitch (mm)</th>
<th>Emitter gap (mm)</th>
<th>Maximum flow rate per emitter (ml h⁻¹)</th>
<th>Maximum flow rate per device (ml h⁻¹)</th>
<th>Maximum flow rate per device’s active length (ml h⁻¹ mm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>5.00</td>
<td>5.0</td>
<td>0.21</td>
</tr>
<tr>
<td>Linear</td>
<td>7</td>
<td>4</td>
<td>4</td>
<td>5.00</td>
<td>35.0</td>
<td>1.46</td>
</tr>
<tr>
<td>Zigzag</td>
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<td>4</td>
<td>2</td>
<td>3.50</td>
<td>24.5</td>
<td>1.02</td>
</tr>
<tr>
<td>Linear</td>
<td>9</td>
<td>3</td>
<td>3</td>
<td>4.00</td>
<td>36.0</td>
<td>1.50</td>
</tr>
<tr>
<td>Zigzag</td>
<td>9</td>
<td>6</td>
<td>3</td>
<td>4.00</td>
<td>36.0</td>
<td>1.50</td>
</tr>
<tr>
<td>Zigzag</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>5.00</td>
<td>15.0</td>
<td>0.63</td>
</tr>
<tr>
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<td>2</td>
<td>4.00</td>
<td>44.0</td>
<td>1.83</td>
</tr>
<tr>
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<td>2</td>
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</tr>
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<td>2.75</td>
<td>46.8</td>
<td>1.95</td>
</tr>
<tr>
<td>Zigzag</td>
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<td>2.4</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zigzag</td>
<td>25</td>
<td>2</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 5. Examples of 3D printed multiplexed electrospinning sources in uniform operation: (a) 9-emitter zigzag array with 6 mm emitter pitch (i.e., 3 mm emitter gap); (b) 9-emitter linear array with 3 mm emitter pitch (i.e., 3 mm emitter gap). When working uniformly, one stable jet per emitter is generated.

Figure 6 shows the per-emitter current versus flow rate characteristics of various multiplexed electrospinning sources with different number of emitters, emitter pitch, and emitter packing. In all the experiments, there is a good correspondence between the data and a least-square power-law fit where the per-emitter current is roughly proportional to the square root of the per-emitter flow rate. Figure 6(a) shows the per-emitter current versus flow rate characteristics of a 1-emitter device, a 7-emitter linear array with 4 mm pitch/gap, a 7-emitter zigzag array with 4 mm pitch/2 mm gap, a 9-emitter linear array with 3 mm pitch/gap, and a 9-emitter zigzag array with 6 mm pitch/3 mm gap. Three interesting trends are shown in the figure: (i) for the same per-emitter flow rate, the devices with a plurality of emitters produce less per-emitter current than the 1-emitter device, evidencing a reduction in the electric field on the emitter spouts due to shadowing by the adjacent emitters; (ii) for a given flow rate per emitter, a zigzag array produces more current per emitter than a linear array of the same emitter pitch and array size; (iii) for dense enough arrays, making the array denser/larger does not significantly reduce the per-emitter current; in addition, each kind of emitter packing seems to converge to a different limit characteristic.

Figure 6(b) shows the per-emitter current versus flow rate characteristics of various zigzag devices, i.e., multiplexed electrospinning sources with 3, 7, 11, and 13 emitters with 4 mm emitter pitch (2 mm emitter gap), and a 17-emitter array with 3 mm emitter pitch (1.5 mm emitter gap). The data suggest that arrays with the same emitter pitch and larger array size emit less per-emitter current, down to a certain limit characteristic. However, the data also suggest that the limit
per-emitter current versus flow rate characteristic varies with the emitter density, i.e., for a given flow rate a device with less distance between emitters (i.e., denser arrays) produce less per-emitter current.

In this study, the largest and densest arrays that continuously operated uniformly had 17 emitters with 1.5 mm emitter gap, which also emitted the largest total flow rate and total flow rate per unit of active length while delivering up to 2.75 ml h\(^{-1}\) per emitter (table 1); in addition, the device produced the smallest per-emitter current for a given per-emitter flow rate. Moreover, the 13-emitter zigzag array with 4 mm emitter pitch was able to deliver almost three times the maximum flow rate ejected by the 3-emitter array with the same emitter packing and pitch. Therefore, the data support the conclusion that multiplexing the emitters is a viable approach to increase the total throughput of electrospinning sources.

### 4.2. Nanofiber characterization

The non-woven mats of aligned nanofibers were collected using 4 different 3D printed devices (a 1-emitter source, and zigzag arrays with 1.5 mm emitter gap and 3, 7, and 17 emitters) while ejecting three different per-emitter flow rates (i.e., 1 ml h\(^{-1}\), 1.5 ml h\(^{-1}\) and 2 ml h\(^{-1}\)); examples of well-aligned nanofiber mats are shown in figure 7, while the histograms from the metrology of the nanofibers are shown in figure 8 grouped per device; a summary of the corresponding statistics is shown in table 2. For the 1-emitter source (figure 8 (a)), the mode diameter is 75 nm and the distributions fairly narrow for flow rates equal to 1 ml h\(^{-1}\) and 1.5 ml h\(^{-1}\); however, for 2 ml h\(^{-1}\), the mode becomes 175 nm and distribution greatly widens with a right-skewed trend. Even though the 1-emitter source can eject significantly more flow rate, the data suggest operating at the lower end of the flow rate range to achieve the thinnest fibers with the narrowest distribution.

**Figure 6.** Per-emitter current versus flow rate characteristics for various arrays. In the plots, \(xL\) is a linear array with \(x\) emitters, and \(xZZ\) is a zigzag array with \(x\) emitters. In a linear array the emitter gap and pitch are the same, in a zigzag array the emitter gap is half the emitter pitch. In figure 6(b), the least-square fit of the 11-emitter and 13-emitter zigzag arrays with 2 mm emitter gap was jointly calculated.

**Figure 7.** Examples of aligned nanofibers generated from a 1-emitter source (a), (b) and zigzag arrays with 1.5 mm emitter gap and 3 (c), (d), 7 (e), (f), and 17 (g), (h) emitters while flowing 1 ml h\(^{-1}\) per emitter.
1-emitter case. Moreover, the 17-emitter array produced for practical purposes the same tight nanofiber distribution (∼81 nm average mean diameter, ∼17 nm average standard deviation) at all flow rates tested in the experiments. Therefore, the data demonstrate that massively multiplexing the emitters in an electrospinning source is a viable approach to greatly increase the throughput of non-woven aligned nanofiber mats without sacrificing the statistics of the nanofibers generated.

Figure 9 shows the dispersity (i.e., ratio between the standard deviation and the arithmetic average) of the nanofiber diameter distributions of the zigzag arrays with 3, 7, and 17 emitters shown in figure 8. In general, the devices with 3 and 7 emitters produce nanofibers with larger dispersity than the device with 17 emitters, although there is no clear trend of which device has associated the smallest dispersity for a given per-emitter flow rate (the 3-emitter device, 7-emitter device, and 17-emitter device have associated the smallest dispersity at 1 ml h⁻¹, 1.5 ml h⁻¹, and 2 ml h⁻¹ per-emitter flow rate, respectively). Nonetheless, the grouping of the dispersity for the 17-emitter device is the tightest, fluctuating around 22% and changing little across the range of flow rates tested. We hypothesize that the difference in the statistics between 3, 7,
and 17-emitter arrays is probably due to the differences in per-emitter current. In figure 6(b), the data suggest that arrays with the same emitter pitch and larger array size emit less per-emitter current for a given flow rate; larger per-emitter current implies larger Coulomb repulsion, causing stronger whipping of the jet, resulting in more statistical variation of the diameter of the nanofiber. In addition, in figure 6(b) the slope of the per-emitter current versus flow rate characteristic is smaller for arrays with the same emitter pitch and larger array size; therefore, differences in the emitter flow rate across the array affect less the uniformity of the emitter current across the array in devices with larger array size. Consequently, the 17-emitter array produces more uniform nanofibers because it has associated the smallest per-emitter current for a given flow rate and the mildest slope of the per-emitter current versus flow rate characteristic.

High-throughput generation of aligned nanofibers is essential to satisfy commercial applications. Parallel emitters distributed along a line have been proposed to increase system productivity; however, to the best of our knowledge this is the first report on multiplexed sources that create mats of aligned nanofibers. For example, Tomaszewski and Szadkowski [31] reported three configurations of stainless steel electrospinning heads that produced PVA nanofibers, i.e., a 26-emitter linear array (75 mm active length), a 26-emitter elliptical array along the perimeter of an ellipse with semi-axes equal to 110 and 60 mm (545.7 mm active length), and a 10-emitter concentric array distributed around the perimeter of a 50 mm diameter circle (157.1 mm active length). The linear array was discarded because only the emitters at the ends of the array were operational; however, the elliptical head produced a total mass flow rate of 11 mg min$^{-1}$ (0.02 mg min$^{-1}$ per mm of active length), and the concentric head produced a total mass flow rate per emitter of 12 mg min$^{-1}$ (0.08 mg min$^{-1}$ per mm of active length). Also, Wang et al reported melt jet electrospinning of polyethylene using an aluminum blade (140 mm active length) that generates 20–25 jets to produce a total flow rate of 80 mg min$^{-1}$ [46] (0.57 mg min$^{-1}$ per mm of active length). Based on the data and the measured density of the PEO solution (1060 kg m$^{-3}$), the maximum mass flow rate of dry fibers that the 17-emitter source can produce is estimated at 33.0 mg min$^{-1}$ (1.94 mg min$^{-1}$ per emitter or 1.38 mg min$^{-1}$ per mm of active length). If the active length of the 17-emitter device would be tiled on the 0.5 m-long active length of the commercial free-surface electrospinning source NS 1S500U Nanospider (ELMARCO, Czech Republic), the total flow rate of the source would be ∼974 ml h$^{-1}$, i.e., it would deplete the 500 ml standard tank in about 31 min, which is 16 times faster than their average continuous run [47].

5. Conclusions

This study demonstrated novel, low-cost, 3D printed, minia- turized, multiplexed electrospinning sources for generation in great quantities of non-woven aligned nanofiber mats using a rotating drum as collector. Two emitter packing versions were investigated: linear arrays, i.e., devices with the emitters deployed along a straight line, and zigzag arrays, i.e., devices with emitters distributed along a line twisting around a straight line. Current versus flow rate characterization of the devices shows that for a given flow rate, a zigzag array produces more current per emitter than a linear array of the same emitter pitch and array size; also, for dense enough arrays, making the array larger does not significantly reduce the per- emitter current.

The largest and densest arrays that continuously operated uniformly, with no dripping, had 17 emitters with 1.5 mm emitter gap, which also ejected the largest total flow rate and total flow rate per unit of active length while delivering up to 2.75 ml h$^{-1}$ per-emitter. The 17-emitter array produced the same tight nanofiber distribution (∼81 nm average diameter, ∼17 nm standard deviation) at all flow rates tried in the experiments (1–2 ml h$^{-1}$ per-emitter); this is strikingly different to the performance shown by 1-emitter sources where the average fiber diameter significantly increased and the statistics notably widened for increasing flow rate. Therefore, the data demonstrate that massively multiplexing the emitters is a viable approach to greatly increase the throughput of non-woven aligned nanofiber mats without sacrificing the statistics of the nanofibers generated. The production of dry nanofibers of the 17-emitter array is estimated at 33.0 mg min$^{-1}$, 1.94 mg min$^{-1}$ per emitter, or 1.38 mg min$^{-1}$ per mm of active length, which compares favorably with the reported multiplexed arrays with emitters distributed along a line.

Several directions for future work on 3D printed multiplexed electrospinning sources are identified. First, without changing the 3D printing technology, the electrospinning sources could be made of more resilient materials, e.g., ceramic [48], to be chemically compatible with a greater variety of feedstock. Second, the emitters could include more complex geometries, e.g., coaxial spouts [39] for hollow nanofiber generation. Third, the great flexibility of the DLP- SLA printing process can yield devices with multi-feedstock feeds; these devices could alternate emitters ejecting different materials that blend into the non-woven mat a plurality of properties, e.g., mechanical reinforcement, self-healing,
transduction, electrical conduction, and cooling, to implement smart nanostructured textiles.

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