Large area uniform electrospun polymer nanofibres by balancing of the electrostatic field

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ABSTRACT

As a technique, electrospinning has been increasingly utilised for polymer nanofibre production, which has a growing list of advanced applications to which they are being applied. However, commercially scaling the process is challenging, especially when the uniformity of the nanofibres across the bulk of the material is important for the required application. At present, most commercially-scalable systems tend to rely on a drum or cylindrical-style electrode, where a multitude of electrospinning jets are formed with no specific controlled distribution or uniformity over its surface. These electrospinning systems also have the drawback of possessing a varying electrostatic field across the length of the electrode, resulting in a range of spinning conditions which result in an inconsistency in the produced nanofibres. Due to the high centrifugal stresses exerted on the polymer during electrospinning, controlling the electrostatic field is crucial for consistent nanofibre production, which forms the basis for applications such as cellular scaffolds and smart materials. In the work reported here, we utilise computational simulation to explore a range of electrode designs to achieve a large area electrospinning system with a balanced electrostatic field across its entire active surface. We demonstrate the output by producing a high-throughput of nanofibres with comparable properties to that of a traditional single spinneret system, but at a processing rate two orders of magnitude faster.

1. Introduction

Electrospinning has been increasingly used for nanofibre production ever since its introduction in 1887 [1]. The electrospinning process was explored in much finer detail in the 1960’s by Sir Geoffrey Ingram Taylor, leading to the iconic electrospinning cone being named the ‘Taylor Cone’ [2]. As of today, electrospinning research and nanofibre markets are extremely large, with the global market increasing from $276.8 million in 2014 to $383.7 million in 2015 [3], and an estimated growth to $2 billion by 2020 [4]. The electrospinning process, which forms nanofibres based on a uniaxial stretching of a viscoelastic solution, utilises electrostatic forces to extend or draw a solution as it solidifies, before being collected onto a targeted substrate [5]. Electrospinning has been successfully used to produce polymer nanofibres for a vast range of applications, including filtration [6], textiles [7], energy (storage/fuel cells/batteries) [8,9], composites [10,11], and biological (cell cultivation, tissue growth and drug delivery) [12,13], to name a few.

Typically, for each application of electrospun nanofibres, specific polymer properties or morphologies are required, such as a specific fibre diameter or crystallinity [14,15]. These parameters are easily controlled when electrospinning using a conventional single needle spinneret, but the process is very slow with the added risk that the needle spinneret will become blocked [5]. In order to apply any nanofibres into a commercially viable application, a scale-up solution needs to be employed. Needleless electrospinning systems are most commonly selected as the solution, as they have numerous benefits over needle-based systems, such as a significantly higher density of electrospinning jets, substantial nanofibre throughput, and a zero chance of needle blockages [16]. However, when the application requires large area uniformity in specific nanofibre properties or morphologies, the importance of the controlled spinning parameters and the uniformity of the Taylor cones is essential.

The design of a needleless system usually involves some form of a large electrode as the main spinneret, which is submerged within a reservoir of the electrospinnable polymer solution. During the spinning process, the electrode is rotated while being subject to a large electrical potential of 30–120 kV [16,17]. As the electrode rotates, the polymer solution forms a thin layer across its surface, which, as a result of the applied high-potential, forms a series of Taylor cones, and subsequent electrospinning jets. The main variation between systems is normally in the electrode design, which has historically seen numerous patents [18–21].
One of the biggest issues with using electrospinning devices of this design, is that they are known to produce nanofibres of inconsistent widths, due to a non-uniform electrostatic field [16]. This is caused almost entirely by the designed shape of the electrode. A non-uniform electrostatic field causes the polymer jets created from different areas of the electrode to be subject to a range of spinning conditions, that include: ejecta accelerations, spinning velocities, centrifugal stresses, all unevenly distributed across the length of the electrode. This results in individual nanofibre diameter, crystallinity and other polymer morphologies varying within the final material, depending on where on the electrode the nanofibre originated.

In this investigation, we use computational software to model the electrostatic fields of numerous electrospinning systems and electrode designs, before finally building and testing the most favourable configuration. We designed each system with the goal of adapting the electrode's structure such that we manipulate the electrostatic field to become uniform across the length of the device, while simultaneously achieving a commercially viable high nanofibre output. In order to maintain nanofibre morphologies, it was equally important to ensure spinning conditions were similar to those when using a single-needle system. An example of this is the inclusion of 'spikes' or raised areas, where a point charge is introduced and as such the electric field is concentrated to a specific location. These point charge sites will promote Taylor cone growth in these intended areas [22], as well as controlling the size of the cone to that of the spike tip. This led to a number of key design implications, which resulted in a patented needleless system [23].

2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO), supplied by Sigma Aldrich, was chosen as the spinnable polymer, with an average molecular weight of ~1,000,000 M_. This was chosen as it is low cost, non-toxic and water soluble. The polymer was used as supplied and not processed any further.

2.2. Solution preparation

A 5% weight fraction solution of PEO in deionized water was prepared at room temperature by magnetic stirring overnight.

2.3. Characterisation

All computational electrostatic simulations were executed using COMSOL Multiphysics 4.4. The electrospun nanofibre morphologies were explored using an FEI Quanta 200F environmental scanning electron microscope (ESEM). The average nanofibre diameters were assessed by measuring every nanofibre observed in several SEM micrographs, all within a defined field of view. No nanofibres were selectively measured or excluded from our data. This was conducted using image processing software ImageJ.

2.4. Electrospinning

The electrospinning setup consisted of a Glassman power supply connected to an in-house built single needle or needleless electrospinning rig. Fig. 1 shows a schematic diagram and photograph of our needleless electrospinning device. In the case of the single needle electrospinning set-up, which is not shown, a simple single needle spinnneret was positioned 15 cm from a rotating collector and charged to +12 kV. The spinning solution was pumped to the needle using a Chemxy OEM syringe pump, at a rate of 700 μl/h.

For the needleless rig, a pinned electrode was manufactured by William R Stewart and Sons to our design. It was constructed of an aluminium drum with approximately 1140 carbon steel pins of length 4.5 mm, spaced 5 mm apart, with a length and diameter of 100 mm. The drum was half submerged within a reservoir of the spinning solution, connected to a motor for rotation. The fluid reservoir was filled with 50 ml of polymer solution for each sample, located opposite to the large rotating collection drum, which was rotated at 8 m/s. The collector was coated with a silicone release paper to allow easy sample removal. The needleless electrode was set at a distance of 15 cm from the collection drum, as this had been previously reported as being the optimum for nanofibre collection [24,25]. Before enabling the high-voltage supply, the electrode's motor was connected to an isolated battery, powering its rotation. The electrospinning voltage was then increased from +20 to 60 kV until Taylor cones were observed forming across the width of the electrode. At this point the spinning voltage was recorded and fixed at that value for the duration of the process.

The atmospheric conditions during electrospinning were controlled by an air handling unit at a temperature of 21 °C, and a relative humidity between 45 and 52%.

3. Theory

3.1. Electrostatics

When designing a cylindrically shaped electrospinning electrode, it is important to start by referring to fundamental physics. Gauss' Law states that excess net electric charge of a conductor resides entirely on its surface [26]. Equally, Coulomb's Law also states that like-for-like charges repel; this means that for a cylindrical electrode, the electric charge will be greatest at each of the furthest opposite ends along the sharpest edge (where the radius of curvature is smallest) [26]. As electrospinning is governed by the magnitude of an applied electrostatic field it is important to avoid any of these unwanted 'hotspots' on the spinning electrode. Previously, where a cylindrical electrode has been used without consideration of the electrostatic field, these field unbalances have been reported, and electrospinning with that device has subsequently produced more nanofibers from the ends of the electrode than in the middle [16]. This was modelled in a simulation to demonstrate graphically the field distribution on these devices, where Fig. 2 displays the resulting electrostatic field produced from a simple cylindrical electrode.

4. Results & discussion

4.1. Computational simulation

In an attempt to prevent any electrostatic field unbalances, a number of different electrode designs were modelled to scale. To access the electrostatic field uniformity, the resulting field strengths were compared between the outside of the electrode, and in the centre, when a potential of +60 kV was applied. Any substantial difference between the two field strengths will indicate an electrostatic field unbalance.

To keep simulation and prototype building simple, as well as maintaining greater control over both Taylor cone size and position, it was decided that a spiked drum would be the starting point for electrode design. In theory, each spike would enhance the electrostatic field and effectively act as a single spinnneret across the electrode surface, in a similar way similar to the traditional single needle electrospinning systems, but with multiple 'needles' on the surface. Each spike of a specific size, positioned uniformly across a drum's surface, would subsequently control where and of what size the Taylor cone is formed by creating focused regions of increased field intensity. This would result in the successful control of the desired polymer morphologies while ensuring uniform fibre deposition.

It is important when using features such as spikes to create point charges, to gain an understanding of how their structure parameters will affect the electrostatic field. Factors such as spike length, aspect
ratio and density, are all critical. For example, if the spikes are located too close to each other, their electrostatic fields would counteract each other, reducing the field strength at the tip; this is called ‘field screening’ [27]. Electrostatic field enhancement can be designed to be in either within a flat field geometries or using protrusions, based on the nano-scale design of surfaces or dielectric inhomogeneity [28,29].

Taking into consideration fundamental physical laws, as well as the desired properties of the final spun nanofibres, numerous electrode designs were simulated, comparing their electrostatic fields. Fig. 3 contains images of the simulations conducted of various different designs. Simulation ‘A’ is a model of a standard spiked electrode. This was designed based on numerous previous spike designs which we observed as having the best aspect ratio without compromising the spike density or the strength of the electrostatic field. With this design, electrostatic field enhancement can be observed to be significantly higher on the spikes furthest from the centre [30]. A demonstration of other spike configurations we explored, such as spike height, can be found in simulation B, here a shorter spike configuration was found to generally reduce the overall strength of the electrostatic field across the electrode. We first explored if reducing the height of the outside spikes would lower the field intensity and even the field distribution (C). This unfortunately resulted in a ‘knock-on’ effect, increasing the electrostatic field strength on the spike next to the reduced height outside spike. Reverting back to the original spike dimensions, we then considered increasing spike separation distance to at least twice that of the spike height, so as to reduce field screening effects (D). This had a significant affect in increasing the strength of the electrostatic field on each spike (where field screening was now minimised), which means electrosprining is possible at much lower applied voltages. However, the uniformity of the electrostatic field was still relatively poor, with no comparable improvement over design A. Additionally, with half the number of spikes (spinnerets) the electrosprining rates will be halved, which is not desired. In another attempt to balance the electrostatic field...
field, the end corners of the electrode were rounded, in an attempt to exploit Coulomb’s law and further concentrate the field on the spikes in the centre (E). This was found to result in the strongest electrostatic field enhancement of all designs, yet despite this, the field was still far from uniform across the length of the electrode.

It was noted, as a common reoccurrence across all of the simulations conducted, that the spikes in-between the ones at either end of the electrode have a generally even field strength. As a result, it was hypothesized that adding additional electrostatic field enhancers to the sides of the electrode, that are not used for electrospinning, would have the same effect. Simulation ‘F’ reveals the effect that these new outside field enhancers have on the electrostatic field distribution. In this case, although the overall field strength is slightly reduced across all of the spikes, the overall field distribution is significantly more uniform across the spinnable area of the electrode. In order to try and increase this effect caused by the outside features, various aspect ratios of the electrostatic field enhancers where probed, which finally resulted in an electrode with a balanced electrostatic field (G).

To allow us to better visualise the electrospinning conditions, a comparison profile of the electrostatic field strengths in configurations A and G, from one end of the electrode to the other (from spike tip-to-tip), can be seen in the plot in Fig. 3. Directly comparing the two profiles highlights the field balancing effects of the external electrostatic field enhancers (disks) added to the outside of the main electrode. A further comparison can be found as an arrow plot in Fig. 4. This plot indicates both field magnitude and direction through each arrow size and direction, illustrating how the field lines from the electrospinning active part of the electrode are both balanced and directed straight towards the collector. This suggests the electrode design will produce an even distribution of polymer nanofibres with a constant morphology. Once we were satisfied with the final simulation design, a prototype was built which can be seen in the photograph in Fig. 1B.

4.2. Nanofibre analysis

Nanofibre samples were produced using a traditional single needle set-up and with two needleless rigs, one with an unbalanced electrostatic field and one with a balanced electrostatic field. To compare the jet behaviour during electrospinning, high-speed images were taken of both needleless set-ups while in operation (Fig. 5). In these photographs, it can be observed how the polymer jets size and path differ between the electrode designs. For the unbalanced electrode (Fig. 5A), the jets are observed to be ‘flaying’ out, predominately originating from the electrode ends, as well as being considerably larger than those originating from the electrode centre. In contrast for the balanced electrode, parallel and uniform jets can be seen across the entire electrode. Recalling the arrow plot in Fig. 4, this result mimics the trends observed in our simulations, which confirms both the effects of an unbalanced electrostatic field on electrospinning and that our balanced design does create a sufficiently uniform field across the electrode surface.

Upon completion of the electrospinning processes using either electrodes, it was immediately apparent how the balanced electrode produced significantly higher quality nanofibres than those created on the unbalanced system. Nanofibre diameter averages and distributions (standard deviations), were sampled by measuring over 100 nanofibres using an SEM. The results for the unbalanced electrode, balanced electrode and single needle system were measured as 150 ± 70 nm, 110 ± 30 nm and 200 ± 30 nm respectively. To illustrate these results graphically, Fig. 6 compares the measured diameters of the nanofibres produced on each system as a histogram.

In the case of the unbalanced electrode, the analysis revealed that the electrospun nanofibres had an average diameter distribution of almost 2.5× greater than those produced with either the balanced needleless electrode or those with the single needle spinneret system. As modelled by the electrostatic field simulations, this broadening effect to the nanofibre diameter range was a result of the stronger electrostatic field located at either end of the unbalanced electrode. This produced significantly thicker fibres from the larger Taylor cones formed at the electrode ends to those formed at the centre. A photograph of this during electrospinning is shown in Fig. 5.

In comparison, the nanofibres produced on the balanced electrode found notable improvements in the diameter uniformity of the nanofibres, with a measured nanofibre diameter distribution of less than half of what was observed on the unbalanced electrode. Most importantly however, the nanofibre diameter distribution was found to be comparable to those formed using a single needle electrospinning set-up, both possessing a standard distribution of 30 nm. Visual comparisons of the nanofibres produced on this electrode revealed cleaner, more consistent sheets of nanofibres, displaying few blemishes such as drip/spit damage on the final material. The area of nanofibre deposition, was significantly more controlled and well distributed, where the jets were observed to travel straight towards the collector rather than flay out (as shown in Fig. 5). This allows for the added feature of targeted nanofibre deposition, which further increases the throughput of the electrospinning apparatus, purely by minimising rogue nanofibres from depositing elsewhere on the rig, thus minimising waste. This confirms that this device would be a suitable alternative for the large-scale production of nanofibres which require the stringent morphologies that currently only single needle set-ups can achieve. This significant improvement to the fibre quality and deposition is attributed to the balancing of the electrostatic field, as well as the overall design of the electrospinning electrode. A photograph of the electrode in operation can be observed in Fig. 7.

It has to be noted that the average nanofibre diameter was smaller for both of the needleless systems than those created by a single-needle set-up. This is not unexpected due to the higher electric potentials applied to the spinnerets. However, this can be controlled via a number of methods, including raising/lowering the applied electric potential, increasing/decreasing the distance to the collector, or changing the viscosity of the solution [31].

To measure the electrospinning processing rate of the balanced electrode and assess its commercial viability, the device was left to electrospin until it had completely depleted all of the solution.
complete 50 ml solution took approximately 1 h to deplete, which is a factor of 72 increase when compared to the original single needle electrospinning. Noting that this device is only 10 cm in length, extending it to 1 m long suggests it could process over 500 ml of solution per hour.

5. Conclusions

Careful consideration and exploitation of fundamental physics have led to the improved design of electrospinning electrodes, which were simulated in COMSOL Multiphysics 4.4. The results from these simulations have led us to a novel electrode design which possesses a fully balanced electrostatic field across the length of the spinnable area of the electrode. This resulted in both the size, position and density of the Taylor cones to be controlled across the electrode’s surface, leading to a greater uniformity, control and deposition in the resulting nanofibres produced. Analysis of resulting nanofibres revealed how the fully balanced electrode produced high-quality nanofibres in a controlled manner, which had an average diameter of $110 \pm 30$ nm. Compared to our original needleless electrospinning system, the diameter spread was $2.5 \times$ times narrower than fibres produced on an unbalanced needleless electrode and almost identical to a traditional single needle set-up.

These investigations ultimately led to the development of a commercially viable working needleless electrospinning prototype which is capable of electrospinning nanofibres of a comparable morphology to those produced by a traditional single needle set-up. The final design has a measured output of 50 ml of solution per hour; a substantial improvement of nearly two orders of magnitude on the previous rate of the traditional single needle system. With the potential to be easily scaled it to 500 ml/h.

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