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High-throughput rod-induced electrospinning

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Abstract

A high throughput electrospinning process, directly from flat polymer solution surfaces induced by a moving insulating rod, has been proposed and demonstrated. Different rods made of either phenolic resin or paper with a diameter of 1–3 cm and a resistance of about 100–500 M Ω , has been successfully utilized in the process. The rod is placed approximately 10 mm above the flat polymer solution surface with a moving speed of 0.005–0.4 m s⁻¹; this causes the solution to generate multiple liquid jets under an applied voltage of 15–60 kV for the tip-less electrospinning process. The local electric field induced by the rod can boost electrohydrodynamic instability in order to generate Taylor cones and liquid jets. Experimentally, it is found that a large rod diameter and a small solution-to-rod distance can enhance the local electrical field to reduce the magnitude of the applied voltage. In the prototype setup with poly (ethylene oxide) polymer solution, an area of 5 cm × 10 cm and under an applied voltage of 60 kV, the maximum throughput of nanofibers is recorded to be approximately 144 g m⁻² h⁻¹.

Keywords: electrospinning, nanofibers, high throughput, free surface

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

1. Introduction

Electrospinning is a simple yet versatile technique to fabricate micro/nano scale fibers for applications in numerous areas, such as flexible electronics (including supercapacitors [1], energy harvesters [2–4], photodetectors [5], lightemitting [6] and transparent electrodes [7]), filtration films [8, 9], battery separators [10, 11], sensors as well as actuators [12–14], tissue engineering [15, 16], drug delivery [17, 18] and catalysts [19, 20]. In particular, properties of electrospun ultrafine fibers (such as ultra-light, multifunctional, continuous and trans-scale capabilities) make them an ideal material to be the building blocks for flexible electronics. The versatility and broad usage of electrospun fibers arise from their high surface area-to-volume ratio, high porosity, and unique optical/chemical/mechanical properties. In general, the traditional single-spinneret electrospinning process has a low production capacity in the range of $0.02 \text{ g} \cdot \text{h}^{-1}$ [21]. In recent decades, researchers have reported numerous approaches to improve the production rate of electrospinning. Multiple-nozzle electrospinning is at the forefront of these techniques to increase productivity; this technique simultaneously produces jets from multiple spinnerets. Nevertheless, experimental results have shown that these positively charged jets would intensively restrain and repel each other if the spinnerets are spaced less than a few centimeters apart [22, 23]. Furthermore, clogging of spinnerets occurs routinely during continuous operations and reduces the overall throughput in the system. An improved version of the multiple-nozzle electrospinning technique utilizes a macroporous polyethylene



Figure 1. (a) A schematic diagram of RIES. (b) An optical photo showing the formation and liquid polymer jets from the flat polymer solution surface under the activation of the rod. RIES process performed at (c) low, (d) normal, and (e) high moving speed of the rod. When the speed is low, the rod acts as the collector where fibers are deposited. When the speed is high, there is insufficient time to generate Taylor cones, resulting in no liquid jets. The arrows represent the direction of rod movement.

tube with distributed micron holes as the emitting electrode; this allows the method o construct multiple liquid jets and reach a production of $5 \text{ g} \cdot \text{h}^{-1}$ [24]. This method, however, still suffers from the issue of clogging. Therefore, there exists a critical need for a clog-free, high throughput electrospinning method.

Electrospinning, without spinneret, could overcome the issue of clogging and maintain continuous production of polymeric fibers [25–29]. For example, Thoppey *et al* [26] used a bowl-shape vessel filled with polymer solution to generate many jets from the edge and increase the throughput to about 40 times higher vis-à-vis to the conventional single-spinneret electrospinning process. Jiang *et al* [28] introduced a microbubble solution system which helped to induce electrospinning from the edges of pyramid spinnerets. NanospiderTM, a pioneering commercial electrospinning equipment, cleverly utilizes liquid solution boxes and moving metal wires to fabricate nanofibers in a continuous manner. These aforementioned high-throughput electrospinning from free polymer solution surface utilized different electrode shapes to enhance local electric field.

It has been previously reported that a high electric field strength of 10^7-10^8 V m⁻¹ is necessary to induce periodic fluctuation and conical spiking for the start of the electrospinning processes [30, 31]. To achieve high electric field strength, a planar electrode is placed into the system ~10 cm above the flat quiescent polymer solution surface. However, the critical voltage will have to exceed ~10³ kV, which is infeasible for this setup. This paper presents a high-throughput electrospinning process from a flat polymer solution surface—rod induced electrospinning (RIES). In RIES, as the grounded phenolic resin or paper rod moves with a speed of 0.005–0.4 m · s⁻¹ a few millimeters above the solution surface back-and-forth, multiple Taylor cones and jets form after the rod passes over the solution surface and starts the electrospinning process. This setup provides several distinct advantages which includes no spinnerets, no clogs, low driving voltage, and ease of scaling up for large-scale fabrication of nanofibers.

2. Experiment section

Polyethylene oxide (PEO) (Mw = 300,000, Dadi Fine Chemical)Co. Ltd, China) was dissolved in the mixture of deionized water and alcohol, at mass ratio of 3:1, to make PEO solution concentrations of 10%, 12% and 14% by mass, respectively. Another 12% concentration with the ratio of 3:2 was also prepared as a comparison. The mixture was sealed and maintained at room temperature for 48h with vigorous stirring. The nanofibers were fabricated by RIES under the temperature of 20-25 °C and a humidity of 40-70%RH. The nanofiber morphologies were characterized by scanning electron microscopy (XL 30, Philips) after sputter-coating with Au at a thickness of 10nm (SCD005, BAL-TEC). An insulation resistance tester (UT513A, UNI-T) was used to measure the resistance of the rod. A resistor of 100 k Ω was connected in series between the ground terminal of the rod and the ground. The current passing through the rod was measured using the test resistor and digital oscilloscope (TDS 2014B, Tektronix). Images of the polymer jets were taken with a digital single lens reflex (DSLR) camera (Canon 500D) with/without home-built telescope.

3. Result and discussion

As illustrated in figure 1(a), the RIES setup consists of an open polymer solution reservoir, an electrically grounded metal collector about 25–40 cm above the polymer solution, a rod made of phenolic resin or paper, and a high voltage power source (GAMMA: ES80P-20W/DDPM). In the prototype experiments, the dimension of the reservoir is $10 \text{ cm} \times 5 \text{ cm} \times 0.5 \text{ cm}$. Figure 1(b) shows an optical photo of many jets generated under the rod with the diameter and



Figure 2. (a) An optical photo showing induced liquid jets on the polymer solution surface as the rod travels leftwards; (b) enlarged view of a single PEO jet; (c) the jetting process from generation to disappearance of a liquid jet during RIES; (d) SEM image of PEO nanofibers deposited on the ground collector; (e) electrical field simulation results on the cross section view around the rod in the RIES: 10 mm in rod diameter, solution-surface-to-rod distance of 5 mm, and 30 kV as applied voltage from the solution to the collector.

length of 1–3 cm and 1 m respectively. As the rod travels a few millimeters above the reservoir at the speed of 0.005–0.4 m \cdot s⁻¹, multiple Taylor cones and jets are quickly generated and some of them become larger as depicted in figure 1(d). If the rod moves too slowly (lower than 0.005 m \cdot s⁻¹), all of the fibers are directly deposited on the rod and not on the collector as shown in figure 1(c). If the speed of the moving rod is fast (higher than 0.4 m \cdot s⁻¹), only a visible protrusion line (whose cross section looks like semi-arc along the rod) appears on the solution surface and moves in the same direction of the rod as illustrated in figure 1(e). Due to the relaxation of the polymer liquid, the protrusion line cannot appear at the surface when the speed is too fast. Therefore there is no fiber deposition on the collector.

In the proof-of-concept experiments, the collector was placed 30 cm above the polymer solution under an applied voltage of several kVs. The rod travelled at 5-10mm above the solution surface at 0.1 m \cdot s⁻¹. It was observed that many tiny jets formed from Taylor cones with a diameter less than 1 mm from the solution directly beneath the rod, as illustrated in figure 2(a). Some jets gradually grew larger with the help of the electrical field and developed into approximately 10 cm long straight and stable jets after the rod had passed (figure 2(b)). The Taylor cones of these large jets were found to be maintained at nearly 2-3 mm in diameter for a few seconds (more than 5s with applied voltage of 30kV) before disappearing as shown in figure 2(c). Correspondingly, at the collector site, bead-free nanofibers were deposited, as shown in figure 2(d). Meanwhile, the smaller jets dissipated within 1 s of their formation and therefore likely did not contribute to the deposition process. Interestingly and unlike in a multiplespinneret electrospinning process, we observed that parallel jets could form within 1 cm of each other from the solution surface with no apparent repulsion. We believe that the absence of the edge effect from the electric field in a spinneret-free RIES process significantly reduced the repulsive Coulomb forces between charged jets.

The introduction of rod, with proper resistance, is believed to greatly improve the local electric field strength under the rod. At an applied voltage of 30 kV and without the grounded rod, the electric field strength between the polymer solution surface and the collector is about 10^5 V m⁻¹—too low to initiate electrospinning. In contrast, when the rod is positioned about 5 mm above the polymer solution surface, the rod can be considered as a 'second ground', in addition to the grounded collector placed 30 cm away. Figure 2(f) shows the result from electric field simulation, where the electric field on the solution surface can reach up to 6.375×10^6 V m⁻¹. At this value, the Coulomb force between the solution and the rod exceeds the surface tension of the solution, giving rise to perturbation on the solution surface that promotes the generation of Taylor cones and assists in the emanation of solution jets.

The behavior of the charge movements was characterized using a resistor of 100 k Ω connected in series between the terminal of the rod and the ground. This resistance was negligible compared to $R_{\rm rod}$, which is at 100 M Ω level. The voltage across the resistor could be detected by a digital oscilloscope to calculate the current across the rod. As illustrated in figure 3(a), when the rod began to skim over the reservoir at a speed of 0.03 m \cdot s⁻¹ at an applied voltage of 25 kV, approximately



Figure 3. In typical experiments, the standard conditions are: the PEO solution concentration is 10 wt%; the applied voltage is 20 kV; the rod diameter is 15 mm; the solution-to-collector distance is 30 cm; solution-to-rod distance is 10 mm; relative humidity is 65%RH; and temperature is 25 °C. The recorded current versus time plots when the rod is passing through with: (a) different applied voltages and speed; (b) PTFE, phenolic resin and paper rods. For (b), the relative humidity is 50%RH and the rod moving speed is 0.03 m \cdot s⁻¹. (c) Critical voltage and resistance of a 30 cm long rod versus rod diameter at a PEO solution concentration of 14 wt%. (d) Critical voltage versus solution surface-to-rod distance.

2–3 charged jets per cm² were induced. Charges from the jets were transferred to the rod, so the current passing through the rod increased sharply from zero to about 80 μ A, and then fluctuated steadily between 80 and 100 μ A. When the applied voltage was lowered to 15 kV, fewer jets were observed and a smaller current was recorded. As the applied voltage decreased to below 10 kV, no liquid jets formed and electrospinning did not occur because the electric field-induced Coulomb force was insufficient to overcome the surface tension of the solution. Based on these observations, we conclude that higher applied voltages lead to more jet formations. On the other hand, the

moving speed of the rod is also an important factor in the RIES process. Figure 3(a) also shows that when the moving speed of the rod was as high as 0.5 m s^{-1} , no jet was observed as there was insufficient time for the fleeting Coulomb force to induce the formation of Taylor cones. There is still a small current peak that occurs at less than 8 μ A around 2.3–2.5 s (maximum current is 7.6 μ A) which may be caused by the movement of dissociated ions in the rod under the strong electric field. Various types of rod materials were tested to induce RIES; however, only phenolic resin and paper worked. As shown in figure 3(b), there were fewer jets and current was smaller with



Figure 4. SEM images of nanofibers produced at different applied voltages: (a) 35, (b) 39 and (c) 43 kV. Standard conditions: solutionto-collector distance of 35 cm, PEO concentration of 12 wt%, solvent ratio of 3:1 (deionized water: alcohol), temperature of 20 °C and relative humidity of 65–70%RH. Scale bar: 1 μ m. (d) Diameter of nanofibers versus applied voltage for a solvent ratio of 3:1. (e) Diameter of nanofibers versus applied voltage for a solvent ratio of 3:2. (f) The throughput of nanofibers versus applied voltages for a solvent ratio of 3:1 and humidity of 50%RH.

a paper rod than that of a phenolic resin rod. It should be attributed to the different resistance of 464 M Ω and 141 M Ω for paper and phenolic resin, respectively. When a polytetrafluoroethylene (PTFE) rod with a higher resistance of about 200 G Ω was used instead, no jets were observed. If the rod resistance was too low, sparks formed between the solution surface and the rod, and the applied voltage was instantaneously decreased due to safety concerns duringthe experiment. This phenomenon has also been reported in the case of air–water interface under planar metal ground electrode [32]. It was also found that when phenolic resin or paper rod absorbed a little amount of water that was sprayed on its surface, it was much easier to induce the generation of jets using this 'wet' rod due to the greatly decreased resistance of the rod. So when the rod picks up water from environment, the resistance decreases too. Considering safety concerns and the thorough volatilization of the solvent, RIES should be kept in an environment with consistently low humidity.

The effects of rod diameter and solution-to-rod distance with respect to the critical voltage to generate jets have also been investigated. As the diameter of the rod increases from 10 to 30 mm, the average critical voltage decreases from 23.7 to 18.1 kV, as illustrated in figure 3(c), indicating an inversely proportional relationship between critical voltage and rod diameter. The reason

is that a rod with a larger diameter has a smaller resistance (the green curve) and charges can go through the rod more easily, which facilitates the generation of jets. Figure 3(d) shows that when the solution-to-rod distance increases from 5 to 20mm, the average critical voltage also increases from 7.1 to 25.8kV with solution concentration of 12 wt%. This is due to the fact that larger solution-to-rod distances will decrease the electrical field under the same applied voltage. Furthermore, a higher average critical voltage is required if the solution concentration increases from 12 wt% to 14 wt%, as higher electrical fields are required to overcome fluid surfaces with higher viscosity.

Using a PEO concentration of 12 wt% with solutionto-collector distance of 35 cm, a temperature of 20 °C and 65–70%RH, solid and smooth nanofibers were deposited under the applied voltages of 35, 39, and 43 kV, as seen in figures 4(a)–(c). Figure 4(d) illustrates the distribution of the diameters of the electrospun nanofibers with respect to the applied voltage at a solvent ratio of 3:1. It was found that the mean diameter of electrospun nanofibers remained uniform between 170–220 nm at this solvent ratio. Figure 4(e) shows that when the ethanol content was raised (solvent ratio = 3:2), the mean diameter of fibers decreased from 460 to 329 nm as the applied voltage increased from 35 kV to 45 kV. We attribute the increase in fiber diameters at higher ethanol content to increased solvent evaporation rate of liquid jets, a significant factor for the RIES process.

Figure 4(f) shows the measured throughputs of nanofibers versus the applied voltage. The throughput data was characterized using the nanofiber mass production per hour divided by the solution area, and each average throughput was calculated from five measured results. RIES was employed for about 15 min for each sample. It was found that the average production of nanofibers increased from $56 \text{ g} \cdot \text{m}^{-2} \text{ h}^{-1}$ to $96.6 \text{ g} \cdot \text{m}^{-2} \text{ h}^{-1}$ when the applied voltage increased from 30 kV to 60 kV, with the largest throughput recorded at $144 \text{ g} \cdot \text{m}^{-2} \text{ h}^{-1}$. To produce more jets with higher velocities, we applied higher voltages which resulted in higher electric field strengths between the rod and the solution surface. As such, faster and high-throughput production of nanofibers was achieved.

There may be two new problems for RIES processing. The first problem is that large open solution surfaces will speed up solvent volatilization, especially toxic solvents, which may result in surface solidification and the reduction of the throughput. A method that adds an additional component is designed to remove the whole thin solution surface online periodically to obtain a fresh solution surface; this might be one of possible solution candidates for RIES processing. The other problem is that the rod will suffer from the coating of fibers in order to decrease the charge transfer ability through the rod; this results in the decrease in the throughput. Therefore a periodical rod cleaning is required.

4. Conclusion

The methodology of high-throughput electrospinning from flat polymer solution surfaces induced by a moving insulating rod has been successfully demonstrated to manufacture nanofibers. Both phenolic resin and paper rods placed in close proximity to a quiescent, open PEO solution are used to induce multiple liquid jets on the solution surface for electrospinning processes. In the proof-of-concept experiments with an open polymer solution of $10 \times 5 \text{ cm}^2$ area, a maximum throughput of nanofibers surpassing $144 \text{ g} \cdot \text{m}^{-2} \text{ h}^{-1}$ at an applied voltage of 60 kV is recorded. The electrospun nanofibers have average diameters of 200-500 nm with good morphology and homogeneous distributions. Experimental characterizations have shown that the critical applied voltage from a free PEO solution surface under the RIES process can be as low as 7.1 kV. As such, RIES provides potential advantages in electrospinning. RIES is a simple, nozzle-free technique that does not clog and is easy to prepare for scale-up productions. At the same time, the relatively fast solvent volatilization for such an open solution area needs to be solved.

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