High scaling ratio line width reduction and fabrication method with electrohydrodynamic jet printing

1 | INTRODUCTION

In recent years, with the development of biological medicine and electronic industry, the demand for making micro-nano structure is gradually increasing. Electrohydrodynamic (EHD) jet printing technology provides an effective and low-cost approach for manufacturing micro-nano structures [1, 2]. This technology has the advantages of wide range of materials application, high printing resolution, no mask required, simple equipment requirement, and it has great potential application in the fields of printing electronics [3–5], biomedicine [6–8], and optical element manufacturing [9, 10].

Polymer materials play an important role in the fields of biomedicine and medical-care [11, 12]. Polymer materials have the advantages of low cost, strong plasticity and easy curing. Thus, polymer structures manufactured by EHD jet printing are worth studying. In the past few years, Sun et al. [13] have fabricated polyethylene oxide (PEO) micro-nanofibers by EHD jet printing technology. PEO is a non-toxic polymer material that can improve the structural strength. Polyvinyl pyrrolidone (PVP) material has good physiological inertia and biocompatibility. Thus, PVP can be used as active material to dissolve matrix carrier rapidly [14]. Both PEO and PVP are synthetic, biocompatible and non-toxic polymer materials, which have been widely used in the field of biomedicine, especially for pharmaceutical development and application as drug excipients [15, 16]. Therefore, in this paper, PEO/PVP mixture was the material chosen for printing, which has good research value.

In the actual printing process, the width of printed line is affected by many factors, such as applied voltage, flow rate, needle diameter, working distance between printing needle tip and substrate, movement speed of the substrate platform and so on. Among them, applied voltage can directly affect the width of the printed line [17–19]. By optimizing the working parameters of voltage, Kim et al. [18] used a needle with an inner diameter of 100 µm to print arrays of line that have the narrowest width of 0.7 µm. The scaling ratio between the inner diameter of needle and the width of printed line is 143.

Flow rate is the critical parameters for the width and uniformity of the e-jet printed lines. The width of ribbons will increase with the increase of its flow rate [20]. However, if the flow rate is smaller or electric field strength is higher, the Taylor cone cannot be maintained, which results in a micro dripping mode [21].

The inner diameter of the needle directly affects the size of the ink droplet, hence it is an important factor affecting the resolution of the printed patterns. Scheideler et al. [22] studied the influence of the nozzle size on the minimum flow rate, and found that the minimum flow rate of the liquid with high viscosity was only affected by the needle size.

Bu et al. [23] studied the influence of movement speed of the substrate platform on the width of moulded lines, and established a relationship between platform movement speed and fibre diameter through modelling method. Finally, a nozzle with inner diameter of 160 µm was used, the lines with width about 4.4 µm were printed, and the scaling ratio between the inner diameter of nozzle and the width of printed line is 36.4. Chang et al. [24] printed PEDOT:PSS lines with width of 27.25 ± 3.76 µm by using a nozzle diameter of 100 µm, and they might be useful for flexible and wearable microdevices. In their work, the scaling ratio is about 4. Park et al. [25] studied the effect of the ratio of applied voltage and working distance on droplet at the needle tip. The needle, a capillary tube with inner diameter of 1 µm, was used to print polymer material lines with 700 nm in width, and the scaling ratio between the inner diameter of needle and the width of printed line is 0.7.

Among them, it is an important goal to obtain a high scaling ratio between the diameter of needle and the printed line width in the printing process. Under the processing condition of high scaling ratio, a needle with relatively larger inner diameter can be used for printing, which is easier to manufacture and can effectively reduce the risk of blockage of the ejected needle in the printing process. At the same time, by reducing the size of the needle diameter, the printing line width with smaller size can be obtained, and it has greater potential for nano-patterns processing. In addition, if the width of the printed line can be predicted in advance, the precise control of the printing process can be realized. Printing on demand will greatly improve the work efficiency.

This paper analyses the key parameters in the printing process, including the influence of movement speed of platform, working distance, applied voltage and flow rate on the printed line width with the cone-jet mode. Working distance here means that the distance between the needle tip and the substrate...
EHD printing system is shown schematically in Figure 1(a). It mainly consists of the following four components. (1) The DC power supply (DW-P602-5F63, Dongwen Company, China): it was used to provide electric field between the needle and the substrate, and its range of output voltage is from 0 to 6000 V. (2) X-Y movement stage with controller (TSA50, Zolix Company, China): the motion distance and speed can be adjusted in both direction of X and Y. The maximum motion distance is 30 mm, and the maximum motion speed is 10 mm/s. Different shapes of motion trajectory can be realized by LabVIEW programming software, such as circular, rectangle, triangles, and spiral etc. (3) The syringe pump (LSP02-1B, Longer Precision Pump Company, China): it was used to fill the material into the needle, and its range of flow rate is from 0.05 µL/h to 150.56 mL/min. Its maximum of the rated linear thrust is more than 180 N. In our experiment, the volume of the syringe was 1 mL. (4) The PC monitor: it was used to control the track of the X-Y movement stage by the LabView software installed on the computer, and observe the output image of the microscope. (5) The Coaxial 1600X industrial microscope (Tuori Weiyi Technology Company, China): its resolution is about 1 µm, and it was used to magnify the printing droplet and observe the morphology of the droplet and cone jet with enlarged images. The experiment equipment of the EHD printing system is shown in Figure 1(b).

In this experiment, PVP (K90) was purchased from Guangdong Yuemei Chemical Co., Ltd., China. PEO (average molecular weight 900 million) was purchased from Guangzhou Lihou Trading Co., Ltd., China. Deionized water was purchased from China Guangdong Qianjing Environmental Protection Equipment Co., Ltd. PVP/PEO mixtures of different mass ratios have different conductivity and viscosity.

### 3 | RESULT AND DISCUSSION

Compared with PVP, the viscosity of PEO is relatively high, so PVP/PEO mixtures with different mass ratios have different characteristics. The most stable state of the mass ratio of PVP/PEO is 8/2, and in our experiment this mass ratio was used to prepare the PVP/PEO mixture. Then the mixture was dissolved in deionized water by using the magnetic stirrer (at a speed of 2000 r/min for 2 h, with temperature 25 °C) to get a kind of compound solution. The compound solution was allowed to stands for 12 h, the bubbles in the solution will disappear. In this compound solution, the mass of PVP/PEO mixture accounts for 12% of the total mass of solution. The viscosity, density and conductivity of the total compound solution are 1.073 Pa s, 1.12 g/cm³, and 10.86 S/m, respectively.

#### 3.1 | Effect of working parameters on the width of printed lines

In the process of EHD printing, four factors including working distance, applied voltage, movement speed of the substrate platform and flow rate, have important influences on the size of printed patterns in the stable cone-jet mode. The working distance is defined as the distance between the needle tip and the substrate. A detailed study will be conducted in the following sections. The cone-jet mode of EHD printing is shown as Figure 2, in which the applied voltage and flow rate were set to 2.0 kV and 0.016 mL/h respectively, and a stainless steel needle with an inner diameter of 890 µm was used.

#### 3.1.1 | Influence of movement speed of the substrate platform on the width of printed lines

In order to study the influence of movement speed of the substrate platform on the width of printed line, the control variable...
method was applied. The working distance was fixed at 1 mm, the applied voltage was set as 2.0 kV, and the flow rate was set as 0.01 mL/h. The platform movement speeds of 3, 5, 8, and 10 mm/s were adopted to print line patterns. It can be seen from Figure 3 that the width of the printed line decreases as the substrate platform moves faster. This is because when the movement speed of the platform increases, the tensile force of the solution on the platform also increases, resulting in the printed lines be stretched and become slender under the combined action of these three forces: electric field, gravity, and surface tension.

In addition, when the movement speed of the substrate platform is too high, the material has not been deposited completely to form patterns. Under this condition, the material will be rapidly stretched, which will lead to insufficient straightness of the patterns. At the same time, the patterns will be carried up by the needle without forming patterns on the substrate. When the movement speed of the platform is too low, the residence time of the accumulated charge in the solution will be increased on the substrate. This will affect the stability of the cone jet, such as shock phenomena occurring during the printing process, which will increase the width of the printed polymer line. Thus, the optimized movement speed of the substrate platform is 10 mm/s.

3.1.2 Effect of working distance on the width of printed lines

In order to study the influence of working distance on the width of printed lines, the movement speed of the substrate platform was fixed at 10 mm/s, the applied voltage was set at 2.0 kV, and the flow rate was set at 0.01 mL/h. Different working distances of 1, 2, and 3 mm were set for printing line patterns. It can be seen from Figure 4, with the increase of working distance, the width of printed line increases. This is because it takes longer time for solvent to dry and evaporate, which cause the e-jet mode changes and the stable Taylor cone cannot be formed in the printing process. In addition, with a constant voltage, the increase of working distance will lead to the reduction of electric field force. This may cause the liquid to be unable to break through the surface tension, which makes it difficult to form the cone jet. Thus, the optimized working distance is 1 mm.

3.1.3 Effect of applied voltage on the width of printed lines

In order to study the effect of applied voltage on the width of printed lines, the movement speed of platform was fixed at 10 mm/s, the working distance was set at 1 mm, and the flow rate was set at 0.01 mL/h. With the increased magnitude of 0.2 kV, the applied voltages ranging from 1.7 to 2.5 kV were adopted to print lines under the condition of stable cone-jet mode. The results of the experiment results were shown as in Figure 5. It can be concluded from Figure 5 that the width of the printed lines decreases with the increase of applied voltage. This is because when the voltage increases, the electric field between the needle and the substrate will be enhanced, which will increase the electric field force on the liquid. Thus, it can break through the surface tension quickly to form the cone-jet flow.
However, when the applied voltage increases to more than 2.0 kV, the process for adjusting parameters to form cone-jet becomes complicated. In the earlier printing stage, shake of cone-jet easily occurs, with uneven or discontinuous lines obtained as shown in Figure 6(a). After a period of adjustment, the cone-jet tends to keep stable slowly. For example, when the applied voltage increases to 2.5 kV, the line width with 860 nm was finally printed, as shown in Figure 6(b).

In order to obtain uniform and continuous lines more conveniently with stable cone-jet mode, it is generally suggested that the applied voltage be set to 2.0 kV.

3.1.4 Effect of flow rate on the width of printed lines

In order to study the flow rate on the width of printed lines, the movement speed of the platform was fixed at 10 mm/s, the working distance was set at 1 mm, and the applied voltage was set at 2.0 kV. With the increased magnitude of 0.002 mL/h, the flow rates ranging from 0.008–0.016 mL/h were adopted to print lines under the condition of stable cone-jet mode. It can be concluded from Figure 7 that the width of the printed line increases with the increase of the flow rate. When the flow rate is 0.008 mL/h, the printed line width is 3.02 µm. As the flow rate is 0.016 mL/h, the printed line width is 6.90 µm. This is because the liquid droplet at the tip of needle also increases with the increase of the flow rate, leading to the larger diameter of the jet flow and the larger width of the printed line.

Compared to the previous studies of the influence of three factors (movement speed of the substrate platform, working distance, and applied voltage) on the width of printed lines, the width of the printed lines were relative smaller in this part of the research work. This is because when the flow rate changes, the waiting time is longer for getting steady flow rate. Thus, the solution of PVP/PEO compound dries easily at the needle tip, and it need to be removed. But after removing the dried PVP/PEO compound, the viscosity of which reflows into the needle tip is lower, and the printed line is smaller.
3.2 Establishment of the function model

In the stable cone-jet mode, the relationship between flow rate and jet diameter of solution with high viscosity and high conductivity satisfy the $Q^{1/2}$ law, which can be expressed as Equation (1) [26]. In Equations (1)–(4), $D_{\text{jet}}$ is the diameter of the jet, $\beta$ is relative permittivity, $Q$ is flow rate, $\varepsilon_0$ is vacuum permittivity, and $K$ is electrical conductivity. PVP/PEO composite solution is a liquid with high conductivity and viscosity. \[(\beta - 1)^{1/2} Q / K\] can be a constant value for PVP/PEO compound. Thus its value, in the present, is supposed to be $a$. We assume that the functional relationship between $D_{\text{jet}}$ and $Q$ is expressed as Equation (2), where $a$ and $b$ are constant coefficients. In addition, in the experiment, we found that $D_{\text{jet}}$ is proportion to the width of printed line $D_{\text{wid}}$. It can be described as Equation (3), where $c$ and $d$ are constant coefficients. By substituting Equation (2) into Equation (3), the function model between the flow rate $Q$ and the width of printed line $D_{\text{wid}}$ of PVP/PEO composite solution can be obtained as shown in Equation (4), where $p$ and $q$ are constant coefficients.

\[
D_{\text{jet}} \approx \left[ (\beta - 1)^{1/2} Q \cdot \varepsilon_0 / K \right]^{1/3} \tag{1}
\]

\[
D_{\text{jet}} = a \cdot Q^{1/3} + b \tag{2}
\]

\[
D_{\text{wid}} = c \cdot D_{\text{jet}} + d \tag{3}
\]

\[
D_{\text{wid}} = p \cdot Q^{1/3} + q \tag{4}
\]

In the cone-jet mode, five groups of flow and the corresponding width values of printed line have been obtained, as shown in Figure 7. The non-linear fitting of function model Equation (4) is carried out by using the curve fitting program of Matlab. The fitting curve of function is shown in Figure 8, where coefficient $p$ is 69.78 and coefficient $q$ is $-0.87$. Thus, the function model Equation (4) is expressed as $D_{\text{wid}} = 69.78 \times Q^{1/3} - 10.87$.

3.3 Experimental verification of the function model

According to the non-linear fitting, the function model between the flow rate and line width of PVP/PEO composite solution is shown in above Equation (4) in the cone jet mode. Here, the correctness of the function model is tested through experiments in the following sections.

In the experiments, the movement speed of the substrate platform is set to $10 \text{ mm/s}$. The working distance is set to $1 \text{ mm}$, the applied voltage is set to $2.0 \text{ kV}$, and four groups of flow rates were set for printing line patterns, as listed in Table 1.

When the flow rate is $0.009 \text{ mL/h}$, the printed line is shown in Figure 9(a), in which the measured line width is $3.62 \mu\text{m}$. When the flow rate is $0.011 \text{ mL/h}$, the printed line is shown in Figure 9(b), in which the measured line width is $4.61 \mu\text{m}$. When the flow rate is $0.013 \text{ mL/h}$, the printed line is shown in Figure 9(c) where the measured line width is $5.58 \mu\text{m}$. When the flow rate is set to $0.015 \text{ mL/h}$, the printed line is shown in Figure 9(d), where the measured line width is $6.38 \mu\text{m}$.

| No. | Flow rate (mL/h) | Calculated line width (µm) | Experimental line width (µm) | Relative errors (%) |
|-----|-----------------|-----------------------------|------------------------------|---------------------|
| 1   | 0.009           | 3.645                       | 3.62                         | 0.7                 |
| 2   | 0.011           | 4.649                       | 4.61                         | 0.8                 |
| 3   | 0.013           | 5.538                       | 5.58                         | 0.8                 |
| 4   | 0.015           | 6.339                       | 6.38                         | 0.6                 |

3.4 High scaling ratio line width reduction

Generally, by EHD printing technology, the scaling ratio of needle inner diameter and printed line width is between 10 and 100 times [19, 27]. To our knowledge, until now, the previous works with scaling ratio higher than 100 is relatively few.
In our experiment, the inner diameter 890 µm of needle was used. By using PVP/PEO composite solution and utilizing the optimized printing parameters, a relatively high scaling ratio of 295 times with line width 3.02 µm was obtained, as demonstrated in Figure 7. Besides, by increasing the applied voltage to 2.5 kV, the higher scaling ratio of 1035 with line width 860 nm was achieved, as shown in Figure 6(a).

When having a high scaling ratio in EHD printing, by employing the same size of needle, a smaller width of line can be obtained. Meanwhile, for obtaining the same smaller width of line, a larger diameter of needle can be employed directly. It can effectively reduce the risk of blockage of the ejected needle in the printing process.

In addition, the diameter of jet is proportional to the square root of the diameter of needle, and the diameter of jet is decreased with the decrease of needle diameter [28]. Therefore, by reducing the size of the diameter of the needle, it has the ability to achieve smaller width of printing line.

4 | CONCLUSION

In this paper, by using the needle with inner diameter of 890 µm, the line width of PVP/PEO composite solution with 3.02 µm was produced by EHD printing technique. The ratio of the inner diameter of needles to the printed line width is up to 295. This is a relative higher scaling ratio in EHD printing. We also established the function model between the flow rate and printed line width of PVP/PEO composite solution.

After experimental verification, the error between the theoretical calculation value and the experimental measurement value of the printed line width is less than 1%. Therefore, the width of the printed line can be predicted in advance by using this equation. The printing process can be controlled precisely to realize printing on demand, which will greatly improve the efficiency of printing. The proposed method and model can provide support for the fabrication and application of micro-nano scale structure.

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E Cheng1,2
Tianxiao Zhang1
Yu Cheng1
Jinnan Li1
Zhengyan Zhang1

1 School of Mechanical Engineering, Hebei University of Technology, Tianjin 300401, China
2 Research Institute for Structure Technology of Advanced Equipment, Hebei University of Technology, Tianjin 300401, People’s Republic of China

Correspondence
Zhengyan Zhang, School of Mechanical Engineering, Hebei University of Technology, Tianjin 300401, China.
Email: zzy@hebut.edu.cn

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