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Print head design and control for electrohydrodynamic printing of silk fibroin

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ABSTRACT

This study investigates the effect of print head design on the electrohydrodynamic printed resolution of silk fibroin. Needles with large orifices measuring at 800 μm were used to build five different print heads. The print heads were manufactured, tested, and optimized using four different silk fibroin solution concentrations of 10 wt.%, 15 wt.%, 20 wt.%, and 22 wt.% at applied voltages that ranged from 10 to 20 kV with two different flow rates of 1.5 μl/min and 2.0 μl/min. Each print head design behaved in a unique manner in terms of printed line characteristics as the flow rate, voltage and concentration were varied. The highest printed resolution of the order of 1 μm was achieved using the pinhole reservoir print head. Possible explanations for each of the observed behaviors and design criteria for future print heads are discussed.

1. Introduction

Ink-jet printing is a powerful technique that affords the user the ability to precisely deposit pre-determined amounts of functionalized materials on a variety of substrates to create either two dimensional surface features or three dimensional structures. Thermal, electrostatic or acoustic mechanisms are used to dispense droplets that are larger than the nozzle size [1–3]. The technique is able to handle picoliters of samples efficiently and without wastage and is thus used widely in the fields of combinatorial chemistry and biology. The low risk of contamination coupled with gentle working conditions has led researchers to investigate its use in tissue engineering, in particular organ and cell printing [4–7]. This efficient handling of minute biological samples also allows the technique to print enzymes, micro-organisms and anti-bodies to create a variety of biological devices and functional biosensors, bioMEMs being the most popular one. It is also used in high throughput experimentation to prepare material arrays for screening and systematic studies for subsequent selection of appropriate materials in a waste efficient and cost effective manner [8].

The limitations of the technology depend and vary on the mechanism of droplet generation. The resolution, range of shear forces within the nozzle and the rheological properties of the ink used are some of the key limitations that are relevant to the current study. In conventional ink-jet printing, low viscosity ink is used to allow for stable flow through the nozzles without the risk of clogging. Similarly the nozzle dimensions need to be sufficiently large enough to allow for particles, macromolecules and isolated cells used in the ink to flow through the aperture without accumulating at the orifice [9,10].

Electrohydrodynamic printing is a new and versatile non-contact direct fabrication technology that is capable of printing at a much higher resolution when compared to conventional ink jet printing [9]. This is made possible by virtue of a large ratio of jet diameter to nozzle diameter which is achievable when an electric field is used to pull out thin continuous micrometer sized jets from a meniscus suspended from the end of the nozzle in the cone-jet mode [11–13]. The two main process control parameters of electrohydrodynamic printing are the applied voltage which is directly proportional to the electric field and the flow rate of the material to be printed, a solution or a suspension of it. The flexibility and processing speed of the technique allow it to compete on cost with conventional lithographic patterning techniques with deposited resolutions reaching the submicrometer and nano-scale dimensions [9].

Ironically the technique's main strength is also its main drawback in terms of jet stability. Varicose and whipping i.e., axisymmetric and non-axisymmetric instabilities and capillary break-up limit the use and effectiveness of the technique. Significant gains have been made recently by Korkut et al. [14] in controlling capillary jets of glycerol and polyethylene oxide (PEO) through the partial neutralization of the surface charges on the jets brought about by the ionization of the gas in the immediate vicinity of the cone-jet. They also reported that the ions produced had a contribution to the final measured current values at the counter electrode [14–17].

Most of the current work are aimed at achieving controlled deposition of various materials with nano-scale dimensions using nozzles with small orifices. Successes have been reported by quite a few research groups with Park et al. [18] generating line widths reaching close to 700 nm using a nozzle with a 1 μm internal diameter. They predicted that improved nano-scale resolutions would be achievable if nozzle dimensions were further reduced. Park et al. also speculated that the electric field concentration brought about by the sharp tips of

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Table 1
Physical properties of silk solutions used in the experiments. All % refer to weight.

Solution	Density (kgm^{-3})	Viscosity (mPa s)	Electrical conductivity ($mS\ m^{-1}$)	Surface tension ($mN\ m^{-1}$)
Formic acid	1220	1.44 ± 0.2	30 ± 2	35 ± 0.3
SF 10%	1310	10 ± 0.2	598 ± 5	40 ± 0.6
SF 15%	1330	18.6 ± 0.2	745 ± 3	42 ± 0.2
SF 20%	1320	29.5 ± 0.1	859 ± 6	44 ± 0.8
SF 22%	1340	39.2 ± 0.2	916 ± 2	45 ± 0.7

the nozzles could help reduce lateral distribution of the jet deployment provided that stand-off heights and applied voltages were kept low. Schrimer et al. [19] were successful in depositing nano dots with diameters close to 200 nm. They also went onto deposit these dots in close succession to produce lines with nanometer widths. This was done using nozzles with sub-micrometer dimensions.

Ferraro et al. [20] employed the use of a pyroelectric effect whereby a lithium niobate crystal substrate is placed near a target substrate and is heated using a focused infrared laser to produce high voltages in the kV range. These voltages elicit an electrohydrodynamic response from a reservoir of solution placed near the target substrate thus drawing out attoliter droplets in the form of a fine jet. They were able to deposit many advanced materials with resolutions reaching 100 nm in line widths. The technique overcomes many of the issues relating nozzle dimensions to the ability to print at nano-scale resolutions. The creation of a virtual nozzle not only makes nano-scale patterning a realistic possibility but also eliminates the need for specialized capillaries or nozzles that are more often than not fragile and prone to clogging up [20–23].

Apart from reducing nozzle dimensions or using specialized equipment there is very little work reported on investigating nozzle design. Li et al. [24] performed a systematic study into the effect of needle tip geometry on the electrohydrodynamic spraying process and reported that the size distribution and liquid relic size significantly reduced with a reduction in needle tip angle.

Wang et al. [25] controlled the jetting frequency by designing a novel retractable needle that was able to deposit both dots and "beads on a string" structures. They varied the flow rate, the concentration of polymer and the frequency of needle oscillation during the printing and established that the jetting frequency shared a close relationship with the retractable frequency of the needle.

Complex protein macromolecules such as silk fibroin are known for their mechanical properties and biocompatibility. The material offers many opportunities in the fields of controlled drug delivery and scaffolds and a recent study conducted by Bayram et al. [26] highlighted the potential for depositing silk fibroin using electrohydrodynamic printing. They successfully printed a variety of intricate patterns at resolutions that varied between 3 and 40 μm depending on the chosen set of parameters. The solution viscosity was identified to be the most important parameter when it came to printing with a flatbed print head [26].

The impracticality of use and the cost of building micrometer and sub-micrometer sized nozzles warrant an investigation into alternative routes to printing with high resolution using nozzles that are cheap to produce, easy to handle and consistent in delivery. The enormous capillary pressures that would have to be overcome in order to use highly viscous materials may also limit the types of feed that could be used in high resolution printing [19]. Thus, the work described in this study is focused on improving print head design in an attempt to achieve high resolution electrohydrodynamic print patterns using silk fibroin.

2. Experimental details

2.1. Materials and silk solution preparation

100 g of de-gummed bombyx silk produced from silk worms of the Bombyx Mori moth was purchased from World of Wool, Huddersfield, UK. 15 g of de-gummed silk was used to prepare 60 ml of silk solution. Formic acid reagent ≥98.0 vol.% and lithium bromide ≥99 wt.% were obtained from Sigma-Aldrich (Dorset, UK).

A weighed amount (15 g) of de-gummed silk fibroin was dissolved in 9.3 M concentration of lithium bromide solution at 70 to 80 °C. The silk solutions were then poured into 30 ml slide-A-Lyzer Dialysis Cassettes (Fisher Scientific Ltd, Loughborough, UK) which suited a molecular weight of up to 3.5 kDa, and dialysed against deionised water for two days to remove the lithium bromide salts in the silk solution. The dialysed silk fibroin solution had a concentration of 8 wt.%. The solutions were then cast into petri dishes and heat dried in an oven at 60 °C until thin, transparent silk fibroin films were produced. The heat dried silk fibroin films were then cut up and weighed before being dissolved in formic acid to produce four different concentrations (10 wt.%, 15 wt.%, 20 wt.%, and 22wt.%) for printing.

2.2. Characterisation of silk solutions

Solution characteristics (density, surface tension, electrical conductivity and viscosity) that are vital to stable electrohydrodynamic jetting were measured. The characterization equipment was initially calibrated before measurements were taken with the silk solutions (Table 1) at the ambient temperature (25 °C), pressure (101.2 kPa) and humidity of (50–55%). The viscosity was measured using Brookfield DV-III Ultra Rheometer for small volumes with a SC4-18 spindle (Brookfield Viscometers Ltd, Harlow, UK). Surface tension was measured using a Kruss tensiometer (Standard Wilhelmy's Plate Method) and electrical conductivity readings were taken using a Jenway 3540 pH/conductivity meter (Bibby Scientific Limited, Stone, UK).

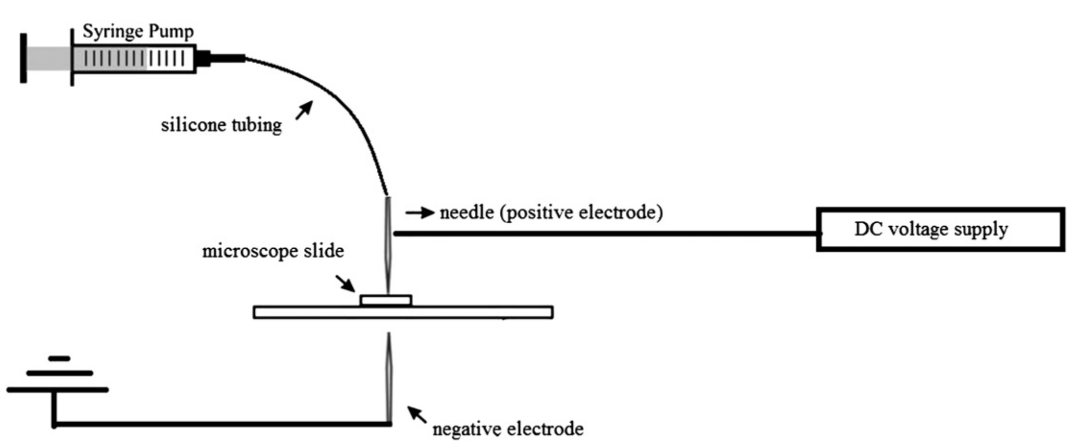

Fig. 1. Schematic diagram illustrating the printing setup.