

2009

# The Effect of Electrode Configuration and Substrate Material on the Mass Deposition Rate of Electrospinning

Jonathan J Stanger  
Nick Tucker  
Andrew Wallace  
Nigel Larsen  
Mark P Staiger, et al.

# The Effect of Electrode Configuration and Substrate Material on the Mass Deposition Rate of Electrospinning

Jonathan Stanger<sup>†‡</sup>, Dr. Nick Tucker<sup>†</sup>, Andrew Wallace<sup>†</sup>, Dr. Nigel Larsen<sup>†</sup>, Dr. Mark P Staiger<sup>‡</sup>, Assoc. Prof. Roger Reeves<sup>\*</sup>

<sup>†</sup> *Biomaterials Engineering and Chemistry, Plant and Food Research Limited, Private Bag 4704, Lincoln, 7608, New Zealand*

<sup>‡</sup> *Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch, 8020, New Zealand*

<sup>\*</sup> *Department of Physics and Astronomy, University of Canterbury, Private Bag 4800, Christchurch, 8020, New Zealand*

Correspondence: jon@jonathanstanger.com

This is the pre-peer reviewed version of the following article: Stanger et. al. 2009 *J. App. Polymer Science* v. 112(3) pp. 1729-1737, which has been published in final form at [DOI: 10.1002/app.29663](https://doi.org/10.1002/app.29663)

## Abstract

Poly(vinyl alcohol) (PVOH) was electrospun using different methods to charge the polymer solution. A positive high voltage relative to the collecting electrode significantly increased the fibre deposition rate. Electron microscopy showed that approximately half of the increase in fibre mass was due to thicker fibres being deposited. The current flowing from the grounded electrode was measured to determine the charge carried on the PVOH jet. This showed that for a positive voltage charging condition there is a much larger current and hence more charge carriers generated in the PVOH solution. As a result, more mass is ejected from the Taylor cone, implying that a positive voltage also produces longer fibre for a given time period. We also tested whether different substrate materials caused any variation when the charging conditions were changed. Statistically significant variation between substrates was only found when the substrate was an insulator and was expected to support a high deposition rate. This confirms the view that the PVOH fibre arrives at the collecting electrode carrying a charge that must be neutralized, otherwise a repulsive charge will form where the fibre is deposited and some fibre will be lost to any alternative earth. In electrospinning, charge carriers are generated using associated redox reactions. Thus, for electrospinning a lack of symmetry in these reactions may result in the generation of different quantities of charge carriers in the PVOH solution and changes in the mass deposition rate of electrospun fibre.

## Introduction

Electrospinning is a low capital way of making nanoscale fibres, defined as having a critical dimension in the nanometre range (1). Electrospinning uses an electrostatic force to draw fibre from a bead of polymeric fluid (2).

While the fibre is in flight it experiences a bending instability (3, 4) leading to a high draw ratio (5). Draw ratio is the ratio of the initial fibre diameter to the final fibre diameter.

The electrostatic force that drives electrospinning was first observed by Gilbert (6), but it took

some 300 years before the implication of Gilbert's observation gave rise to serious quantitative research. The first work on modelling the process followed from Zeleny's (7) examination of fluid drop behaviour under the influence of high strength electrostatic fields. This was extended by Taylor (2, 8, 9) in his analytical treatment of the eponymous cone. Later developments (4, 10-12) used a finite element approach to quantify the bending instabilities experienced by the fibre in flight.

Cooley (13) and Formhals (14) made unsuccessful early attempts at commercialisation of the electrospinning process. In the past two decades, the technique was rediscovered as a comparatively simple way to produce small quantities of ultra-fine fibres. For an extended discussion of different methods of producing ultra-fine fibres refer to *An Introduction to Electrospinning and Nanofibres* (1). Generally, the low mass deposition rate limits the possible range of applications to niche markets. Consequently, only a small number of companies currently use electrospinning commercially, for example in specialist filtration elements and wound dressings or electrospinning equipment<sup>1</sup>.

Compared with traditional macro-scale fibre production techniques, electrospinning has several advantages. Electrospun fibres can be made with diameters <100 nm in a continuous process (15). It has also been observed that the draw ratios of the fibres are very large (5). The high draw ratio can induce increased crystallinity in the resulting fibre (16). Hence, fibres produced via this method are expected to have a tensile strength approaching their theoretical maximum. The high surface area to volume ratio of electrospun materials can be used for medical dressings, drug delivery and active filtration (17, 18).

The arrangement of research electrospinning apparatus is typically a horizontal syringe pump with a needle held at high voltage in proximity to an earthed electrode (the collector) (1). The apparatus provides a simple route to the production of small quantities of fibre (see Figure 1).

<sup>1</sup> Example companies include Donaldson Filtration Solutions Ltd., eSpin Technologies Inc. Electrospinz Ltd and NICAST Ltd.

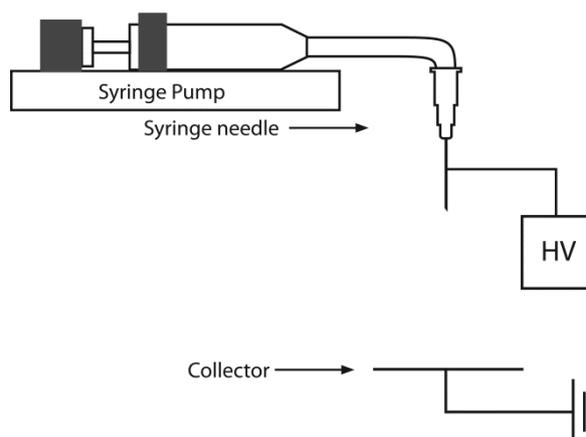


Figure 1: Schematic of essential elements to a typical electrospinning apparatus.

The main process parameters that affect electrospinning (19) are summarised in Table 1. Studies have been made of solution properties (19-24), process parameters (16, 21, 25-27) and ambient properties (19, 28). A significant challenge in the study of electrospinning is the interdependent nature of the processing parameters. The large number of interacting parameters makes it difficult to combine existing research for the development of large scale, commercial electrospinning techniques.

We observed that when the charging conditions were reversed (i.e. high voltage was moved from needle to collector) there was a significant decrease in the deposition rate of fibre. Originally, it was expected that the change in charging conditions would only result in the change of the sign of the charge on the two electrodes and hence have no effect on the deposition rate. This paper reports on our observation of the decrease in deposition and an examination of the cause. We also demonstrate a simple method of optimisation for single jet operation using electrostatics and for the optimisation of larger multiple jet operations.

## Experimental

### *Electrode Configuration*

The primary independent variable being examined in all experiments was the electrode configuration. This refers to changing the method of inducing charge on the electrodes used in the electrospinning process. Two electrode configuration pairs were used in our experiments. The first pair used a positive high voltage power supply to charge the collector electrode and a connection to ground to charge the polymer solution. This was compared with using a positive high voltage to charge the polymer

# The Effect of Electrode Configuration and Substrate Material on the Mass Deposition Rate of Electrospinning

Solution Properties	Process Parameters	Ambient Properties
Concentration	Electrostatic Potential	Temperature
Viscosity	Electric Field Strength	Humidity
Surface Tension	Electrostatic Field Shape	Local Atmosphere Flow
Conductivity	Working Distance	Atmospheric Composition
Dielectric Constant	Feed Rate	Pressure
Solvent Volatility	Orifice Diameter	

Table 1: Processing parameters that affect the electrospinning process.

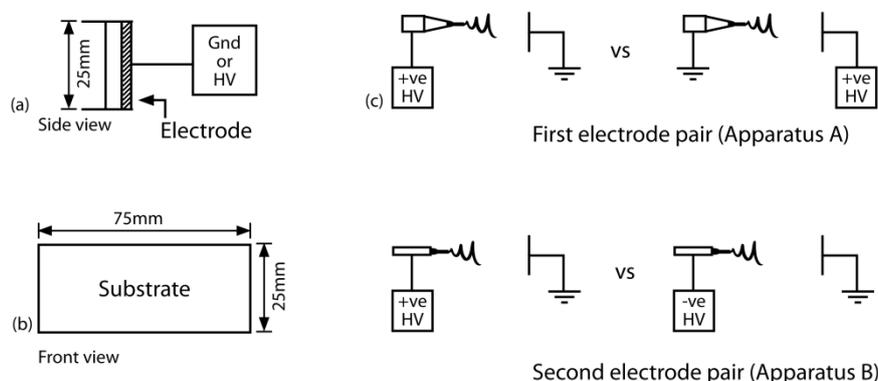


Figure 2: (a) Substrate positioning (b) Substrate dimensions (c) Electrode configurations used.

solution and a connection to ground to charge the collector. The second pair used a negative high voltage power supply to charge the polymer solution and a connection to ground to charge the collector electrode. This was compared with a positive high voltage to charge the polymer solution and a connection to ground to charge the collector electrode. These different electrode configurations are summarised in Table 3 and Figure 2.

### Substrate Variation

A secondary independent variable also examined in some of our experiments was the effect of different substrate materials placed over the copper collector electrode on the collection of electrospun fibres. We used a range of substrates with different dielectric constants and conductivities. The relevant properties for the substrate materials used are summarised in Table 4 (29).

### Dependent Variables

The primary dependent variable measured was the mass deposition rate. This was taken to be the raw mass of fibre deposited on a substrate per hour. Each mass deposition rate was calculated from the weight change of the substrates used. This was measured using a Mettler-Toledo AG204 balance reading to 0.0001 g.

One secondary dependent variable measured was the current flow in the electrospinning fibre. This was taken to be the current flowing between ground and the electrode connected to ground. Current measurements were obtained using a

Keithley Instruments 610B Electrometer (Cleveland, OH, USA). The Electrometer was placed in series with the grounded electrode when measuring the current flow to protect it from high voltages.

Another secondary dependant variable measured was the fibre diameter. This was calculated using image analysis software applied to images produced by a Field Emission Electron Microscope. The electron microscope used was a JEOL JSM-7000F (Jeol Co., Tokyo, Japan) field emission scanning electron microscope (FESEM). FESEM micrographs were taken with a voltage of 2 kV to prevent residual charge building up on the polymeric fibres. Each sample of fibre was taken from a 10-second deposition. When gold sputtering was performed the short deposition time allowed for a thin fibre mat which ensured a uniform gold coating.

The final secondary dependent variable measured was the initial jet diameter. This was measured using an optical USB microscope model QX5 (Digital Blue Corporation, Georgia, USA) operating at 60 x zoom and calibrated using a standard calibration slide.

### Apparatus

#### Apparatus A

The apparatus used was an Adam series electrospinning apparatus (Electrospin Ltd, Blenheim, New Zealand) (see Figure 3). This apparatus used the typical electrospinning arrangement of two electrodes, one acting as a

collector and the other in contact with the polymer solution. The two electrodes were mounted in a horizontal arrangement on a linear rail and aligned such that their centres shared a common axis. The collector electrode was a copper plate 25 x 25 mm which substrates could be placed over. The spinning tip was an Axygen T-200-Y 200  $\mu\text{L}$  pipette tip with an orifice diameter of 0.8 mm and a copper tube 30 mm long and 3 mm diameter placed in line with the pipette tip to charge the polymer solution. A stable spinning jet was maintained by controlling solution pressure at the spinning tip by raising or lowering the height of the solution header tank whilst observing the needle with the USB microscope (model QX5, Digital Blue Corporation).

#### Apparatus B

This apparatus used a variation on the typical electrospinning arrangement, via a parallel plate arrangement with one plate as a collector and the other plate charging the polymer solution as it flowed through to the metal spinning tip (a 21 gauge syringe needle) (see Figure 4). Both parallel plates acting as the electrodes were circular disks of aluminium with a diameter of 100 mm and a thickness of 8 mm. These plates were mounted using three acetyl rods placed every  $120^\circ$  around the edge of the plates ensuring a common axis at the centre of the electrodes. The polymer was charged using an EW series high voltage power supply (Glassman High Voltage, INC.). The polymer solution flow rate was controlled with a KD Scientific model 100 syringe pump.

#### Solution Properties

The polymer used in this work was poly(vinyl alcohol) (PVOH) purchased from BDH Chemicals (VWR International) ID# 297914D. The polymer has a molecular weight of approximately  $115,000 \text{ gmol}^{-1}$  and an 87% minimum degree of hydrolysis (DH). The polymer was dissolved in distilled water at an average concentration of  $9.66 \times 10^{-4} \text{ molL}^{-1}$ , taking 2 hrs at  $80^\circ\text{C}$  with constant stirring. A dilution of  $4.58 \times 10^{-4} \text{ molL}^{-1}$  was used in the following experiments. The density of the final solution was measured to be  $1013 \text{ kgm}^{-3}$  using a Metler-Toledo XS105 microbalance with specialist density measuring kit. The conductivity of the final solution was measured to be  $365 \mu\text{S}$  using the conductivity meter described by (30). The dielectric property of the solution is assumed to be the same as the solvent

Positively Charged Solution	$E_0$
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	-0.34 V
$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ $[\text{OH}^-] = 10^{-8} \text{ molL}^{-1}$	-0.40 V -0.87 V
$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ $[\text{H}^+] = 10^{-6} \text{ molL}^{-1}$	-1.23 V -0.88 V
Negatively Charged Solution	$E_0$
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ $[\text{H}^+] = 10^{-6} \text{ molL}^{-1}$	0.00 V -0.35 V
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ $[\text{OH}^-] = 10^{-8} \text{ molL}^{-1}$	-0.83 V -0.34 V

**Table 2: Redox reactions that might be possible at the spinning head and the associated potentials including those adjusted for approximate solution ion concentration.**

i.e.  $\epsilon=78.4$ . A series of possible redox reactions that might occur at the spinning head have been summarized in Table 2.

#### Experimental Methods

##### Experiment 1

This experiment examined the mass deposition rate as a function of the substrate material and electrode configuration. Each substrate was cut to 25 mm x 75 mm. The three substrates examined were standard glass microscope slides, sheets of 100 type N (phosphor doped) silicon wafer and 0.8 mm thick steel. The first pair of electrode configurations was used (Table 3 and Figure 2).

The production of fibre was done on apparatus A. The substrate was 50 mm from the pipette tip. The high voltage power supply was set to deliver 11.5 kV. At this voltage the electrode configuration could be changed and still supply a stable spinning environment without having to alter the supply voltage. For each combination of substrate material and electrode configuration, two samples were produced by depositing fibre for 10 minutes. From these samples the mass deposition rate was measured and averaged to give one value for each combination of substrate material and electrode configuration.

##### Experiment 2

This experiment measured the fibre diameter, initial jet diameter and the current flow as a function of the electrode configuration. Fibre samples were produced by depositing for 10 s

Collector Electrode	Polymer Solution
“First pair” Positive High Voltage (+ve) Ground (Gnd)	Ground (Gnd) Positive High Voltage (+ve)
“Second pair” Ground (Gnd) Ground (Gnd)	Negative High Voltage (-ve) Positive High Voltage (+ve)

**Table 3: Summary of the different electrode configurations used in this paper.**

## The Effect of Electrode Configuration and Substrate Material on the Mass Deposition Rate of Electrospinning

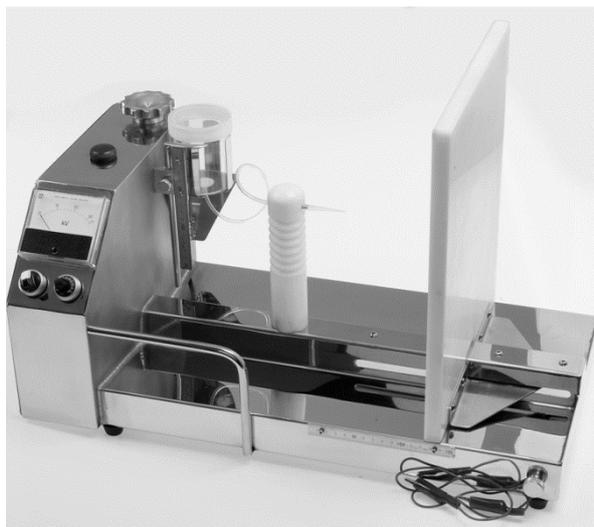


Figure 3: Photograph of Electrospinz Adam Series electrospinning apparatus (microscope not shown for clarity).

onto an aluminium foil substrate. The electrode configurations used were the first pair (Table 3 and Figure 2). After these samples were obtained the deposition was continued and the initial jet diameter and current flow was measured. The initial jet diameter was measured as described in the dependent variables section. The current flow was measured between a ground source and the electrode connected to ground in the method described in the dependent variables section.

The production of fibre was done on apparatus A. The substrate was 50 mm from the pipette tip. The high voltage power supply was set to deliver 11.5 kV. At this voltage the electrode configuration could be changed and still supply a stable spinning environment without having to alter the supply voltage.

### Experiment 3

This experiment measured the mass deposition rate as a function of the electrode configuration. The electrode configurations used were the second pair (Table 3 and Figure 2). For the electrode configuration collector (Gnd) / solution (-ve) five samples of fibre were collected. For each electrode configuration collector (Gnd) / solution (+ve) seven samples of fibre were collected. Each sample was the result of 10 minutes of deposition.

Apparatus B was used to produce the fibre. The substrate used was aluminium foil of dimensions 60 mm x 60 mm. The substrate was 100 mm from the needle tip. When the polymer solution electrode was charged to a negative potential the flow rate required for a stable Taylor cone was 0.32 mL/h, whereas when the electrode was

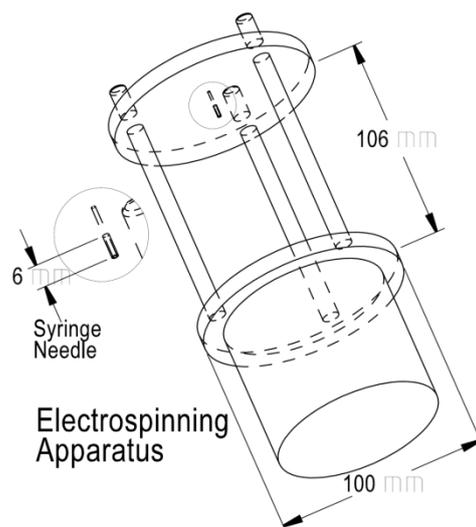


Figure 4: Schematic of apparatus B shown with an isometric tilt to demonstrate detail.

charged to a positive potential the flow rate required was 0.62 mL/h. The high voltage power supply was set to deliver 33 kV. At this voltage, stable spinning could be obtained for both electrode configurations.

## Analysis and Discussion of Results

### Experiment 1

This experiment served as an initial examination of possible substrate effects on the deposition rate (Figure 5). The chosen substrates covered both a range of dielectric constants and conductivities (Table 4). The results presented in Table 6 and Figure 5 were obtained by performing an ANOVA for two factors (substrate and electrode configuration) with repeats on the raw data for experiment 1. Differences between treatments were compared with the Least Significant Difference (LSD) calculated for the 5% level of significance. This has the property that differences between treatment means are statistically significant at the 5% level if they exceed the LSD(5%) (31). These results demonstrate that the electrode configuration is the primary source of variation ( $P < 0.001$ ), with steel and silicon collectors in the collector (Gnd) / solution (+ve) configuration depositing at an average of 4.4 times the rate of the collector (+ve) / solution Gnd) configuration. However both the substrate ( $P = 0.005$ ) and the interaction between factors ( $P = 0.018$ ) are also statistically significant sources of variation. Figure 5 shows that glass with a configuration of collector (Gnd) / solution (+ve) has a deposition rate only about two thirds of the rate with silicon and steel substrates (12 mg/h less,  $P < 0.05$ ), while the

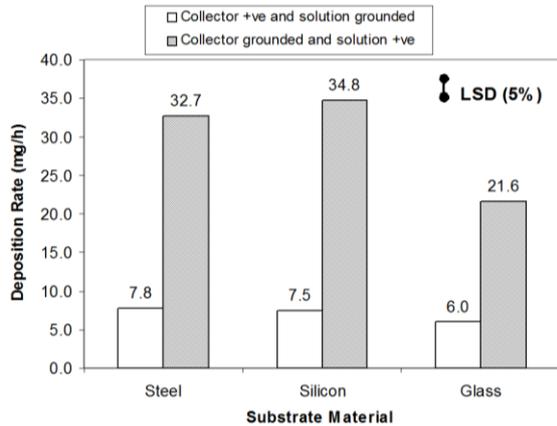


Figure 5: Average mass deposition rates measured for experiment 1. Differences between means are statistically significant at the 5% level if they exceed the LSD (5%).

Material	Dielectric Constant	Conductivity
Aluminium	$\infty$	$3.6 \times 10^7$
Steel	$\infty$	$1 \times 10^7$
Silicon	11.5	$1.6 \times 10^{-3}$
Glass	3.8	$1 \times 10^{-12}$

Table 4: Physical properties of the substrate materials.

deposition rates with collector (+ve) / solution Gnd) are similar across the 3 substrates ( $P > 0.05$ ). Thus the differential response to glass when the polarity of the electrodes is reversed is the main source of the variation due to interaction. The physical cause of this variation is that, when the larger mass throughput is required, the low conductivity of the glass becomes a significant limiting factor. Hence the charge flow across the substrate is being limited, allowing the charge on incoming fibre to build up and repel new fibre.

**Experiment 2**

Using the average fibre diameter measured from images such as Figure 6 (see Table 5) it is possible to use equation 1 (right) to calculate the factor by which the volume changes for the

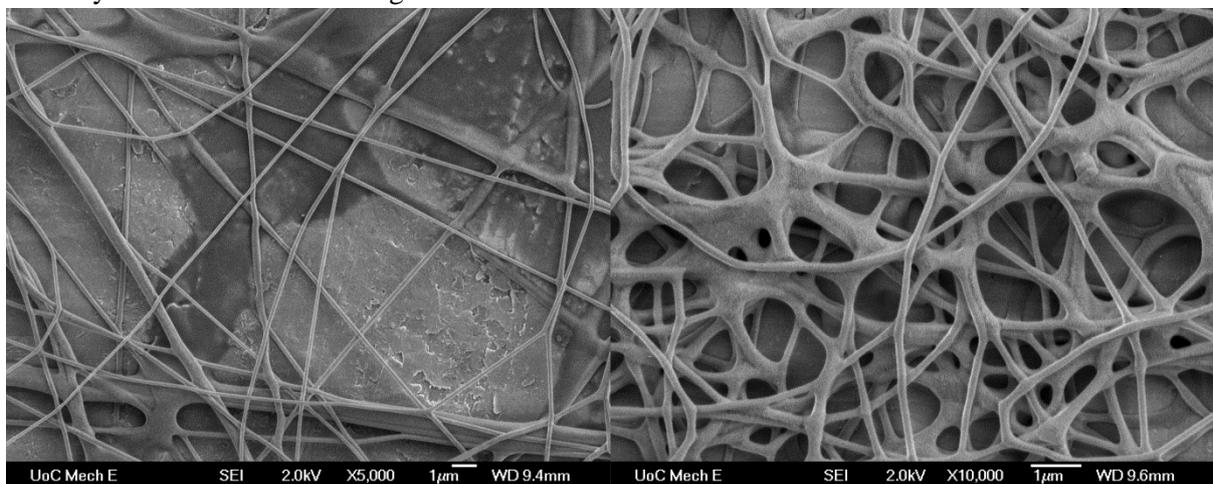


Figure 6: Example FESEM images used to measure the final fibre diameter.

Electrode Configuration	Initial Jet Diameter (m)	Fibre Diameter (m)	Current Flow ( $\mu A$ )
Collector (+ve) Solution (Gnd)	$1.22 \times 10^{-5}$	$1.7 \times 10^{-7}$	0.30
Collector (Gnd) Solution (+ve)	$3.52 \times 10^{-5}$	$2.8 \times 10^{-7}$	0.85

Table 5: Values of the dependent variable measured in experiment 2.

Source of Variation	Degrees of Freedom	Mean Squares	Variance ratio	F probability
Substrate	2	$6.43 \times 10^{-5}$	14.29	0.005
Electrode Configuration	1	$1.53 \times 10^{-3}$	340.00	<0.001
Interaction	2	$3.82 \times 10^{-5}$	8.49	0.018
Residual	6	$4.50 \times 10^{-6}$		
Total	11			

Table 6: ANOVA results for the raw data in experiment 1.

deposited fibre onto an aluminium collector when the electrode configuration is changed. The increase in volume of fibre produced using an electrode configuration of collector (Gnd) / solution (+ve) is a factor of 2.7 times the volume obtained by using a configuration of collector (+ve) / solution (Gnd). This is compared to an increase in mass deposition rate by a factor of over 4 for the same electrode configurations using steel and silicon substrates.

$$V = \pi r^2 l \tag{1}$$

where V is the volume of fibre [ $m^3$ ], r is the average radius of fibre [m], and l is the length of fibre [m].

## The Effect of Electrode Configuration and Substrate Material on the Mass Deposition Rate of Electrospinning

The results from Table 5 allow the calculation of further parameters describing the state while electrospinning is active. Equations 2 and 3 can be solved to give the total velocity of the fibre while in flight. These equations are modified from (5). Note that this velocity is the length of the vector summation of both the tangential “whipping” velocity and the parallel velocity of fibre travelling toward the collector. Additionally using the velocity in equation 3, equation 4 can be solved to give the charge per unit length when the fibre contacts the substrate. These values are summarised in Table 7.

$$v_1 = \frac{w_1}{\rho_1 \pi r_1^2 t_1} \quad (2)$$

where  $v_1$  is the velocity of the aqueous jet [ $\text{ms}^{-1}$ ],  $w_1$  is the weight of solution used [kg],  $\rho_1$  is the density of the polymer solution (measured to be  $1013 \text{ kgm}^{-3}$ ),  $r_1$  is the radius of the polymer jet [m], and  $t_1$  is the time spent spinning the fibre [s].

$$v_2 = \frac{w_2}{\rho_2 \pi r_2^2 t_2} \quad (3)$$

where  $v_2$  is the spinning velocity when the fibre hits the substrate [ $\text{ms}^{-1}$ ],  $w_2$  is the weight of the fibre on the substrate [kg],  $\rho_2$  is the density of the spun fibre ( $1260 \text{ kgm}^{-3}$ ),  $r_2$  is the radius of the spun fibre [m] and  $t_2$  is the time spent spinning the fibre [s].

$$\sigma = \frac{I}{v_2} \quad (4)$$

where  $I$  is the current flow in the circuit formed by the electrospinning apparatus [A],  $v_2$  is the velocity when the fibre hits the substrate [ $\text{ms}^{-1}$ ] and  $\sigma$  is the charge per unit length on the fibre as it hits the substrate [ $\text{Cm}^{-1}$ ].

### Experiment 3

One objection to the results obtained so far is that they have used the ground as the source of negative charge. As the ground is not a true negative charge source the experiment was repeated using a convertible power supply so that the effects of a negative charge can be directly compared to a positive charge. The positive charge solution deposited at  $35\text{mg/hr}$  compared to  $16.4\text{mg/hr}$  with the negatively charged solution. Performing ANOVA on the raw data showed that the variance due to charge polarity is significantly larger than the variance of the data and hence there is a significant effect due to the charge polarity used on the polymer solution.

Electrode Configuration	Initial velocity of fluid in jet $v_1$ ( $\text{ms}^{-1}$ )	Velocity of fibre at substrate $v_2$ ( $\text{ms}^{-1}$ )	Charge per Unit Length $\sigma$ ( $\text{Cm}^{-1}$ )
Collector (+ve) Solution (Gnd)	0.30	63	$4.75 \times 10^{-9}$
Collector (Gnd) Solution (+ve)	0.20	130	$6.56 \times 10^{-9}$

Table 7: Summary of results from equations 2, 3 and 4.

### Substrate Effects

Analysis of experiment 1 reveals that not all substrates share the same behaviour. Figure 5 shows that using glass substrates will result in a significant decrease in the mass deposition rate. It is proposed that the conductivity of the glass substrate is low enough to hinder the neutralisation of the charges on incoming fibre. This would result in a build-up of a charge on the substrate that would repel the incoming fibre similarly to that proposed by (32). Silicon, however, has a high enough conductivity to perform as well as the metals. Hence, it is proposed that if a substrate material has a conductivity below a critical value then the deposition rate of fibre in electrospinning will decrease. This critical value however will depend on the charge density on the fibre and the mass deposition rate and hence will be different for almost all electrospinning conditions. A detailed exploration of the exact critical value has not been undertaken in this work.

### Effect on Deposition Rate

The results of these experiments clearly show that as the electrode configuration is changed there is a change in mass deposition rate. Application of a positive high voltage to the polymer solution must generate a positive charge on the solution. In all experiments, this results in a higher deposition rate. Application of a negative high voltage to the solution in experiment 3 has similar results to the application of ground to the solution in experiment 1, where a metallic substrate was also used. The application of ground in these cases must be acting to generate a negative charge to counter the positive charge generated by the high voltage power supply. With all other factors held equal, changing the charge polarity should simply result in the reversal of the electric field direction. However, the reversal of the electric field direction should have no effect on the mass deposition rate. Hence as shown in experiment 2 there must be a different quantity of charge being generated, depending on the charge polarity. This would result in a difference in the forces being

exerted on the polymer solution and hence the difference in the mass deposition rate.

It should be noted, however, that the results from experiment 3 cannot be directly compared with the results of the other two experiments as ground cannot act as a perfect negative supply. Unless the grounded electrode is essentially the only object that can act as ground in an effective infinite space then other ground sources will also generate a negative charge. This charge is proportional to the distance from the high voltage electrode and as such in an apparatus as described in this paper would be small. However, even a small charge will reduce the efficiency of the grounded electrode acting as a negative supply. Due to this low efficiency, the results in the first two experiments will be partly due to a change in the electrostatic field between the two electrodes. Hence, direct comparison between the results of the two different electrode configuration pairs is unsound; however, the trend is still obvious in all experiments. Further discussion of the electric field effects on the mass deposition rate are beyond the scope of this paper.

Examination of literature relating to electrospraying (33-35), a process related to electrospinning, shows that these processes can be viewed as a simple redox cell (34). A redox reaction typically consists of a pair of reactions, a reduction involving a species gaining an electron and an oxidation involving a species losing an electron (36). This is driven either by the energetic favourability of the products or by forcing a current to flow through the solution. Electrospraying and electrospinning are electric current driven processes. At the positively charged electrode, an oxidation reaction occurs and conversely at a negatively charged electrode a reduction reaction occurs. This results in a net flow of charged species, completing the electrical circuit. In this treatment there is no free surface charge, all charge is carried by the species generated in the redox reactions.

If there was a lack of symmetry in the redox reactions that occur, then dependent on the polarity of the charging electrode there would be a different quantity of charge carriers produced. This change in the quantity of charge carriers would be mirrored in the mass deposition rate because the charge determines the force on the solution. If there was a higher charge generated for one of the charge carrier polarities then it is

expected that there would be a significant difference in the velocity that the fibre would reach in flight.

Therefore, it is proposed that the change in the mass deposition rate is due to a higher capacity for positive charge carriers to be generated than negative charge carriers in a PVOH solution. Experiment 2 shows that there is a significantly higher final velocity when a positive charge is used, which is expected from equation 5 below (37) if a higher charge is generated. The initial velocity of the fluid jet also supports this claim as the conditions where there is a higher charge should result in a larger mass being expelled from the Taylor cone (2). As the larger mass has had little time to take advantage of its higher charge and accelerate in the electrostatic field it should have a slower speed. Furthermore, it is well known that like charges repel (37) and as such during the jet thinning process if the jet held a higher concentration of charge the final fibre will be thicker. This is due to the charge on the jet forcing the surface outward, countering the jet thinning. The draw ratio of the fibre in question also shows that the generation of a positive charge results in less jet thinning. Finally, the current measurements in experiment 2 directly show the higher charge when a positive source is used to charge the polymer solution.

$$F = Eq \quad (5)$$

where  $F$  is the force experienced by a charged object [N],  $E$  is the electric field [V/m] and  $q$  is the charge on the object [C].

These conclusions reflect the same conclusions reached by previous authors (38-40) using polyamide-6 or polyacrylonitrile. However, here this discussion links the observed differences to the generation of charged species in situ (as accepted in electrospraying (34)) rather than charged species generated in the solution preparation.

### Conclusions

The substrate material has no effect on the mass deposition rate in an electrospinning process unless the material's conductivity is below a critical value. Insulating materials will allow a repulsive charge to build up on the substrate, decreasing the mass deposition rate.

The generation of a positive charge in a solution of water and PVOH with a copper electrode results in a higher quantity of charge carriers

# The Effect of Electrode Configuration and Substrate Material on the Mass Deposition Rate of Electrospinning

than the negative case. The generation of charge carriers is explained using work done on the analogous process of electrospraying. The higher quantity of charge carriers causes a lower draw ratio and thicker fibres but a larger quantity of fibre is produced and a higher final speed upon deposition.

## Acknowledgements

We would like to thank the University of Canterbury for their help with equipment; particularly Mike Flaws for his assistance with the FESEM, the New Zealand Institute for Crop & Food Research for hosting this research and providing financial support, the Foundation of Research, Science and Technology for financial support through their Technology for Industry Fellowship program, and ElectrospinZ Ltd, 44 Lee St, Blenheim, New Zealand ([www.electrospinZ.co.nz](http://www.electrospinZ.co.nz)) who supplied the electrospinning machine.

## References

- 1 Ramakrishna S, Fujihara K, Teo W, Lim T, Ma Z. An Introduction to Electrospinning and Nanofibers. World Scientific, 2006.
- 2 Taylor G. Electrically Driven Jets. Proc Royal Soc London A: Mathematical, Physical & Engineering Sciences 1969; 313: 453-475.
- 3 Reneker DH, Yarin AL, Fong H, Koombhongse S. Bending instability of electrically charged liquid jets of polymer solutions in electrospinning. J App Physics 2000; 87:4531-4547.
- 4 Yarin AL, Koombhongse S, Reneker DH. Bending instability in electrospinning of nanofibers. J App Physics 2001; 89: 3018-3026.
- 5 Wang H, Shao H, Hu X. Structure of Silk Fibroin Fibres Made by an Electrospinning Process from a Silk Fibroin Aqueous Solution. J App Polymer Sci 2005; 101: 961-968.
- 6 Gilbert W. De Magnete, Magneticisque Corporibus, et de Magno Magnete Tellure (On the Magnet and Magnetic Bodies, and on That Great Magnet the Earth), London, Peter Short, 1628.
- 7 Zeleny J. The Electrical Discharge from Liquid Points, and A Hydrostatic Method of Measuring the Electric Intensity at their Surfaces. Physical Rev 1914; 3: 69-91.
- 8 Taylor G. Disintegration of Water Drops in an Electric Field. Proc Royal Soc London A: Mathematical, Physical & Engineering Sciences 1964; 280: 383-397.
- 9 Taylor G. The force exerted by an electric field on a long cylindrical conductor. Proc Royal Soc London A: Mathematical, Physical & Engineering Sciences 1965; 291: 145-158.
- 10 Hohman MM, Shin M, Rutledge G, Brenner MP. Electrospinning and electrically forced jets. I. Stability theory. Phys Fluids 2001; 13: 2201-2220.
- 11 Hohman MM, Shin M, Rutledge G, Brenner MP. Electrospinning and electrically forced jets. II. Applications. Phys Fluids 2001; 13: 2221-2236.
- 12 Yarin AL, Koombhongse S, Reneker DH. Taylor cone and jetting from liquid droplets in electrospinning of nanofibers. J App Physics 2001; 90: 4836-4845.
- 13 Cooley JF. Apparatus for electrically dispersing fluids, United States of America 692631, February, 1902.
- 14 Formhals A. Process and Apparatus for Preparing Artificial Threads, United States of America 1975504, 1934.
- 15 Sundaray B, Subramanian V, Natarajan TS, Xiang R-Z, Chang C-C, Fann W-S. Electrospinning of continuous aligned polymer fibers. App Phys Lett 2004; 84: 1222-1224.
- 16 Zhao S, Wu X, Wang L, Huan GY. Electrospinning of Ethyl-Cyanoethyl Cellulose/Tetrahydrofuran Solutions. J App Polymer Sci 2004; 91: 242-246.
- 17 Shanmugasundaram S, Griswold KA, Prestigiacomo CJ, Arinze T, Jaffe M. Applications of Electrospinning: Tissue Engineering Scaffolds and Drug Delivery System 2004: 140-141.
- 18 Tsai PP, Schreuder-Gibson H, Gibson P. Different electrostatic methods for making electret filters. J Electrostatics 2002; 54: 333-341.
- 19 Mit-uppatham C, Nithitanakul M, Supaphol P. Ultrafine Electrospun Polyamide-6 Fibers: Effect of Solution Conditions on Morphology and Average Fiber Diameter. Macromol Chem Phys 2004; 205: 2327-2338.
- 20 Fong H, Chun I, Reneker DH. Beaded nanofibers formed during electrospinning. Polymer 1999; 40: 4585-4592.
- 21 Jarusuwannapoom T, et al. Effect of solvents on electrospinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers. Eur Polymer J 2005; 41: 409-421.
- 22 Shenoy SL, Bates WD, Frisch HL, Wnek GE. Role of chain entanglements on fiber formation during electrospinning of polymer solutions: good solvent, non-specific polymer-polymer interaction limit. Polymer 2005; 46: 3372-3384.
- 23 Wannatong L, Sirivat A, Supaphol P. Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene. Polymer Internat 2004; 53: 1851-1859.
- 24 Zeng J, Xu X, Chen X, Liang Q, Bian X, Yang L, Jing X. Biodegradable electrospun fibers for drug delivery. J Control Release 2003; 92: 227-231.
- 25 Deitzel JM, Kleinmeyer J, Harris D, Beck Tan NC. The effect of processing variables on the morphology of electrospun nanofibers and textiles. Polymer 2001; 42:261-272.
- 26 Mo XM, Xu CY, Kotaki M, Ramakrishna S. Electrospun P(LLA-CL) nanofiber: a biomimetic extracellular matrix for smooth muscle cell and endothelial cell proliferation. Biomaterials 2004; 25: 1883-1890.
- 27 Zhong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B. Structure and process relationship of electrospun bioabsorbable nanofiber membranes. Polymer 2002; 43:4403-4412.
- 28 Casper CL, Stephens JS, Tassi NG, Chase DB, Rabolt JF. Controlling Surface Morphology of Electrospun Polystyrene Fibers: Effect of Humidity and Molecular Weight in the Electrospinning Process. Macromolecules 2004; 37: 573-578.
- 29 CRC-Press. CRC Handbook of Chemistry and Physics, Cleveland, Ohio, CRC Press, 2004.
- 30 da Rocha RT, Gutz IGR, do Lago CL. A low-cost and high-performance conductivity meter. Journal of Chemical Education 1997; 74:572-574.
- 31 Snedecor GW, Cochran WG. Statistical Methods (7th ed.), The Iowa State University Press, Ames, Iowa, 1980.
- 32 Liu L, Dzenis YA. Analysis of the effects of the residual charge and gap size on electrospun nanofiber alignment in a gap method. Nanotechnology 2008; 19: 355307-355314.
- 33 Berkel GJV, Kertesz V. Redox buffering in an electrospray ion source using a copper capillary emitter. J Mass Spectrom 2001; 36: 1125-1132.

- 34 Blades AT, Ikonomou MG, Kebarle P. Mechanism of Electrospray Mass Spectrometry. Electrospray as an Electrolysis Cell. *Anal Chem* 1991; 63: 2109-2114.
- 35 Wilhelm O. Electrohydrodynamic spraying - Transport, mass and heat transfer of charged droplets and their application to the deposition of thin functional films, Doctor of Sciences, Swiss Federal Institute of Technology, Zurich, 2004.
- 36 Chang R. Chemistry. McGraw Hill, 1998.
- 37 Halliday D, Resnick R, Walker J. Fundamentals of physics. New York, John Wiley & Sons, 2001.
- 38 Mit-uppatham C, Nithitanakul M, Supaphol P. Effects of Solution Concentration, Emitting Electrode Polarity, Solvent Type, and Salt Addition on Electrospun Polyamide-6 Fibres: A Preliminary Report. *Macromol Sympos* 2004; 216: 293-299.
- 39 Supaphol P, Mit-uppatham C, Nithitanakul M. Ultrafine Electrospun Polyamide-6 Fibers: Effects of Solvent System and Emitting Electrode Polarity on Morphology and Average Fiber Diameter. *Macromol Material Eng* 2005; 290: 933-942.
- 40 Sutasinpromprae J, Jitjaicham S, Nithitanakul M, Meechaisue C, Supaphol P. Preparation and characterization of ultrafine electrospun polyacrylonitrile fibers and their subsequent pyrolysis to carbon fibers. *Polymer Internat* 2006; 55: 825-833.