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Insights into the power law relationships that describe mass deposition rates during electrospinning

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Abstract

This work explores how in electrospinning, mass deposition rate and electric current relate to applied voltage and electrode separation, factors give a range of applied electric fields. Mass deposition rate was measured by quantifying the rate of dry fibre deposited over time. Electric current was measured using a current feedback from the high voltage supply. The deposition of fibre was observed to occur at a constant rate for deposition times of up to 30 min. Both the mass deposition rate and electric current were found to vary with the applied voltage according to a power law. The relationship between the electric current and mass deposition rate was found to be linear for all combinations of applied voltage and electrode separation. This means that for all combinations of applied voltage and electrode separation, hence for all applied electric field conditions, there is a constant charge density of 96.1 C/kg for PVOH.

Introduction

Electrospinning has been established as a valuable method of producing micro- and nano-scale continuous fibres [1]. Electrospinning uses high strength electric fields (> 1 kV/cm) to form jets of fluid polymer and then draw them into nanometre diameter fibres [2]. The application of high voltage causes charging of the droplet formed at the tip of the spinneret. The accumulated charge results in the droplet deforming into a Taylor cone from which mass is ejected in the form of a fluid jet [3]. At some distance along the jet, an “instability” forms that causes the jet to follow an expanding helical path. Consequently, the fibre is greatly stretched,

and drawn down to a nanometre scale diameter [4].

Typically, the fibre or mass deposition (or production) rate or flow (or feed) rate has been treated as a parameter that can be varied independently [5-6]. However, a constant internal pressure within the Taylor cone must be maintained to allow stable electrospinning from the Taylor cone that in turn establishes a constant flow rate [7]. It is possible, when studying the process in a quasi-stable state, to treat the mass deposition rate as a response variable related to processing conditions (such as voltage, electrode distance, humidity, polymer concentration,

conductivity...) [8]. Treating mass deposition rate as a response variable, it has been shown that both the mass deposition rate and electric current observed at the collector have a power law relationship to the applied voltage [8-10]. Existing reports have only varied the applied voltage to study the effect of different magnitude electric fields on the electric current at the collector electrode and the mass deposition rate. Hence it is impossible to distinguish between an effect due to applied voltage and an effect due to applied electric field.

This work aims to relate variation in mass deposition rate and electric current at the high voltage electrode to corresponding variation in distance between the spinneret and the collector plate in addition to applied voltage. In addition this work attempts to determine if there is a relationship between mass deposition rate and electric current flow. This relationship could be used to determine valid charge densities for use in theoretical modelling of the process. Mass deposition rate is measured as the amount of dry material deposited on the collector plate over a given time. When stable electrospinning is occurring this mass is entirely in the form of a nano-fibre. If the process is unstable, then spots of liquid polymer or sprayed particulates may also be deposited. The data presented in this work will extend the empirical understanding of the relationship between processing variables and the resultant fibre, to control of the process.

Experimental materials and methods

Electrospinning was carried out using an aqueous solution of poly(vinyl alcohol) (PVOH) (Chemiplas NZ limited, Wellington, NZ). The PVOH had an average molecular weight of 118,000 gmol^{-1} and degree of hydrolysis (DH) in the range of 85-90%. The stock polymer solution was prepared by dissolving PVOH in distilled water for approximately 2 hrs at 60°C with constant stirring at 500 rev/min using an overhead stirrer. To take in account any loss of solvent during the dissolution process, the stock polymer concentration was determined by drying a small sample in a convection oven at 80°C to find the weight of solids. This information was used to dilute the stock polymer solution to an accurate final concentration of 8 wt%.

The electric current flow was quantified by measuring the current flowing into the high voltage electrode in contact with the polymer solution. Throughout the experiments the

solution properties were kept constant. The variable used to control the electrospinning process was the internal fluid pressure inside the Taylor cone – this pressure is varied by raising and lowering the header tank. By controlling the internal pressure it was possible to obtain a stable Taylor cone and hence obtain comparable results between different voltages and distances.

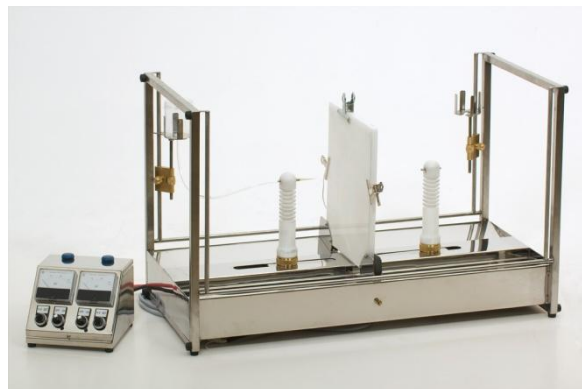


Figure 1: Photo of the Electrospinz ES4 electrospinning apparatus.

All samples were electrospun using a Model ES4 electrospinning apparatus (Electrospinz Ltd., New Zealand) as shown in Figure 1. The polypropylene pipette tip used was an Axygen T-200-Y 200 μL pipette tip with an orifice diameter of 0.5 mm. The processing parameters were measured to an accuracy of ± 1 mm for the working distance, ± 250 V for the potential difference and ± 0.5 mm for the head height allowing determination of hydrostatic pressure. Conductivity of the polymer solution was measured using a Eutech PC 510 conductivity meter.

The mass deposition rate was determined by depositing fibre onto collector electrodes made of cleaned, nominally 150 mm square sheets of 316 stainless steel connected to earth via a magnetic holder. After fibre deposition, samples were dried for 8 hrs (RH 40%, 25°C) before analysis. The mass deposited on each steel electrode was weighed using a 4 figure balance (Mettler Toledo AG204, measurement error of ± 0.0001 g). For each set of voltage and distance conditions three replicates were produced by depositing fibre for a period of 1, 2, 3, 5, 10, 20 and 30 minutes.

Electric current was measured using a compactDAQ data acquisition platform (cDAQ-9172 with 9205 and 9263 modules, National Instruments) connected to a Glassman high voltage power supply. The compactDAQ

platform was able to program a ramping voltage from just above the onset of electrospinning (typically ~5kV) to an upper limit (~20kV) in 0.5kV steps every 5s. During this time the current feedback output was logged with the 16 bit ADC module at a sampling rate of 1kHz. The data was processed using a custom MATLAB script to provide the average current drawn for a given voltage. Fluid pressure was adjusted by varying the height of the polymer header tank to maintain stable electrospinning throughout.

Results and Discussion

This paper investigates the response of the mass deposition rate and the electric current drawn by the high voltage electrode to the applied electric field. For a given voltage and distance the mass deposited on the collector electrode increases linearly with time. Figure 2 shows the increase in mass of fibre deposited over time on the collector. The gradient of the linear trend is the mass deposition rate. The linear relationship means that there is a constant rate of mass deposition over a period of up to 30 min. The y-intercept at $t=0$ is not at zero mass due to the interaction between the stainless steel electrode and the magnet used to hold it in place. A 316 stainless steel plate that is connected and removed from the magnetic specimen holder without having electrospun fibre deposited on it will apparently gain an average of 0.005 g due to residual magnetism, which corresponds to the magnitude of the y-intercept observed.

	75 mm	100 mm	125 mm
7.5 kV	$6.70 \times 10^{-6} \pm 0.26 \times 10^{-6}$	$3.63 \times 10^{-6} \pm 0.06 \times 10^{-6}$	$2.59 \times 10^{-6} \pm 0.18 \times 10^{-6}$
10.0 kV	-	$6.30 \times 10^{-6} \pm 0.12 \times 10^{-6}$	-
12.5 kV	-	$15.99 \times 10^{-6} \pm 0.08 \times 10^{-6}$	$9.08 \times 10^{-6} \pm 0.10 \times 10^{-6}$
15.0 kV	-	$20.70 \times 10^{-6} \pm 0.11 \times 10^{-6}$	-

Table 1: Mass deposition rate (g/s) for a range of voltages and electrode distances where each value represents the constant linear deposition rate over time - as seen in Figure 2. The errors listed are the standard error obtained from the linear regression performed to find the linear mass deposition rate.

Observations of the electric current at the high voltage electrode shows that the electric current increases with a power law relationship to voltage. Figure 3 shows a typical electric current responses to step increases in voltage. The trace is started approximately at the initiation voltage for electrospinning which is why the current is near zero. Traces were recorded for the electric current response to applied voltage at electrode distances of 75, 100, 125 mm. The relationships between electric current and applied voltages at the three electrode distances were deduced to be in the form of the power law.

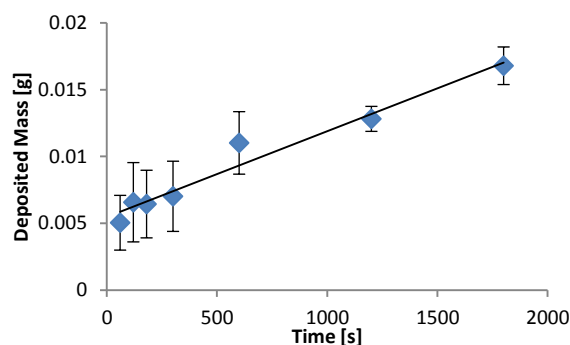


Figure 2: Mass increase of collector electrode over time with a fixed electrode distance of 100 mm and fixed applied voltage of 10 kV. The error bars represent one standard deviation of the measured data. The trend line equation is $m = 6.41 \times 10^{-6} t + 5.49 \times 10^{-3}$ ($R^2 = 0.964$).

The mass deposition rate was determined at 100 mm distance for the voltages 7.5, 10, 12.5 and 15 kV, and at 75 mm and 7.5 kV with 125 mm and 7.5 and 12.5 kV (Table 1). Increasing the voltage or decreasing the distance between electrodes leads to an increase in the mass deposition rate. This is consistent with the expectation that the flow rate at the Taylor cone would increase with electric field strength. Past studies have only considered varying the applied voltage [8-10]. This study offers the possibility of examining the response in terms of the applied electric field. This can be done as varying the electrode distance at a constant applied voltage varies the applied electric field in a similar but more sophisticated manner to simply varying the applied voltage.

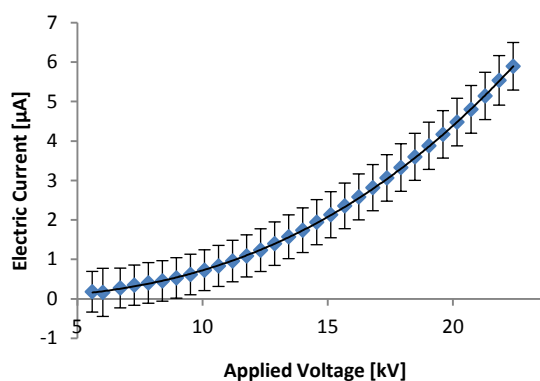


Figure 3: Observed electric current at the high voltage electrode in response to applied voltage at the fixed electrode distance of 100 mm. The error bars represent one standard deviation of the measured data.

deviation of the measured data. The trend line is described by $I = 0.00182 V^{2.60}$ ($R^2 = 0.998$).

The three traces that were recorded allow the identification of the electric current being drawn under the same conditions that each mass deposition rate was observed at (Table 2). Like the mass deposition rate, the electric current increases with applied voltage and decreasing electrode distance. Thus the electric current increases with increasing electric field, as expected if it is assumed that the polymer fluid is a conductive fluid; the conductivity of PVOH was measured to be $400 \mu\text{S}/\text{cm}$. However the power law relationship seen in Figure 3 suggests that the flow of charge at the Taylor cone is not purely conductive in the sense of $I = \sigma E$, but that the current (I) must include other terms related to the electric field (E), with higher powers.

	75 mm	100 mm	125 mm
7.5 kV	0.432 ± 0.516	0.333 ± 0.513	0.284 ± 0.515
10.0 kV	-	0.711 ± 0.515	-
12.5 kV	-	1.281 ± 0.545	1.026 ± 0.558
15.0 kV	-	2.073 ± 0.581	-

Table 2: Electric current measured at the high voltage electrode (expressed in μA) for a range of voltages and electrode distances.

Using the data presented in Table 1 we can look at the relationship between mass deposition rate and the applied voltage which for a fixed distance linearly relates to electric field strength. These results are shown in Figure 4. A linear relationship ($R^2 = 0.962$) would fit with this data but a power law ($R^2 = 0.972$) provides a slightly better fit. However with only four data points the difference in fit is negligible but since previous literature has reported several examples of power law relationships in similar circumstances for various polymers (polyurethaneurea, polyacrylonitrile and PVOH) [8-10] it is reasonable to assume a power law relationship. Figure 5 shows the relationship between the mass deposition rate and increasing distance while the applied voltage is kept constant.

Where the relationships between electric current, flow rate and applied voltage are studied specifically for PVOH [9], it was found that there were power law relationships between the applied voltage and mass flow rate or electric current [9]. The response of current to applied voltage was $I = cV^c$ where c is a constant. Compared to the exponent reported in Figure 3 of 2.60 there is a significant difference. The

relationship between flow rate and applied voltage was not directly measured but determined algebraically as $Q = cI^c$ from the reported relationship between electric current and flow rate [9]. Since the exponent is less than 1 this means the function has a decreasing gradient with respect to increasing applied voltage. This is contrary to other reported observations including that shown here in Figure 4 where the flow of mass increases with respect to increasing applied voltage.

To explain the differences between the relationships for PVOH, first note that all reported relationships were relative to electric current measurements [9]. The results reported here differ from previously published work because the electric current is measured at the high voltage electrode rather than at the connection between the collector electrode and earth. This allows examination of what is happening at the Taylor cone without considering the possibility of charge loss processes interfering with the results [11]. Depending on the electrode geometry used, measuring electric current at the collector electrode can give significantly different results to a simultaneous measurement of the current drawn at the Taylor cone. This may account for the discrepancy in the power law exponent as the higher voltages may result in a higher chance of discharge ions reaching the collector plate. Further, the results here were recorded using a constant pressure polymer feed system where the pressure supplied matches the pressure generated by surface tension and surface charge at the Taylor cone. If a constant volume flow rate feed system is used it is possible to under- or over-feed the Taylor cone resulting in flow rates that do not represent stable electrospinning. The ability to achieve stable electrospinning underpins the work described in this paper, and lack of stability may account for the discrepancy between the observed power law exponents.

The other two comparable reports in literature used polyurethaneurea (PUU) [8] and polyacrylonitrile (PAN) [10] respectively. The relationships for PUU were found to be $I = cV^c$ and $Q = cI^c$. The relationships for PAN were found to be $I = cV^c$ and $Q = cI^c$. As no errors are given for the exponents the fact they are very similar implies the relationships for electric current are in good agreement with that shown in Figure 3 where the exponent is 2.60. Both papers report a faster response of flow rate

to applied voltage than was observed in Figure 4 - as indicated by the higher exponents. However, both papers also report a linear relationship between electric current and flow rate such as that observed in Figure 7. For a linear relationship to exist the exponents must be similar across the range reported suggesting the faster response of flow rate to applied voltage may be an artefact of the curve fitting algorithms used. The exponents may be closer to that observed in Figure 4, however only further experiments can determine this. The good agreement between the results for two entirely different polymers [8,10], despite the disagreement from previous PVOH results [9] suggest that these relationships may be valid for a wide range of expected electrospinning conditions and hence close to a general rule.

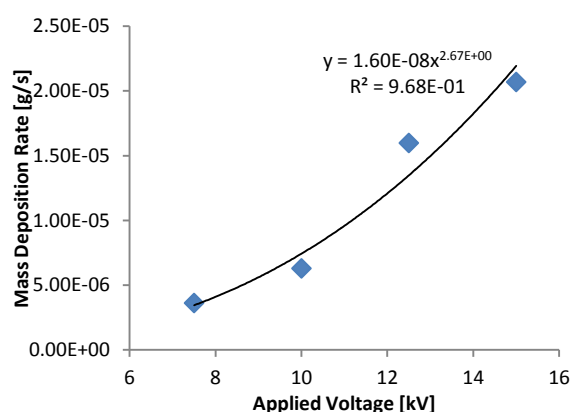


Figure 4: Mass deposition rate response to applied voltage for the fixed electrode distance of 100 mm. The trend line is described by $m_{rate} = 1.60 \times 10^{-8} kV^{2.67}$ ($R^2 = 0.972$). Error bars representing the standard error obtained from the linear regression as presented in Table 1 are smaller than the marker for each data point.

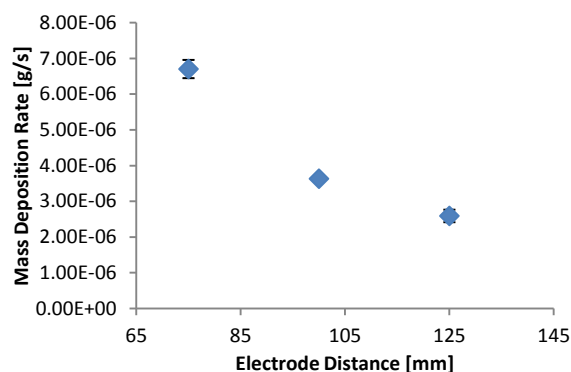


Figure 5: Mass deposition rate response to electrode distance for a fixed applied voltage of 7.5 kV. Error bars representing the standard error obtained from the linear regression as presented in Table 1 are shown where some are smaller than the marker for the data point.

The nature of the electric field formed in a typical needle-flat plate electrospinning apparatus is difficult to quantify. Hence, reports

in literature often use the infinite parallel plate approximation to estimate the electric field strength that then drives the properties of the electrospinning process [12]. The data may appear to indicate that the response varies with a parallel plate capacitor approximation of the electric field; however Figure 6 shows that this is not a valid approach. The three different mass deposition rates for a single electric field condition (Figure 6) show that this representation of the field is not a valid description of the phenomenon. This cluster of three distinctly different deposition rates at 1 kV/cm indicates that although mass deposition rate responds to electric field strength the relevant electric field strength is not related to the parallel plate approximation.

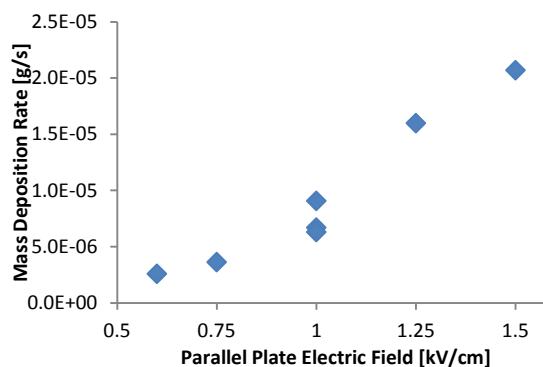


Figure 6: Mass deposition rate plotted against the parallel plate approximation of electric field strength. Note the cluster of points at 1 kV/cm resulting from the failure of the parallel plate approximation in representing the electric field strength. Error bars representing the standard error obtained from the linear regression as presented in Table 1 are smaller than marker for each data point.

In Figure 3 a power law relationship between electric current and applied voltage is found with an exponent of 2.60. As has already been shown (Figure 4) the relationship between mass deposition rate and applied voltage is also a power law with an exponent of 2.67 (Figure 4). The similarity of the exponents suggests that the response of the mass deposition rate and electric current to the applied electric field may be related to each other. As the relevant magnitude of the applied electric field may not be simply determined (Figure 6) plotting mass deposition rate against electric current for all points recorded allows the comparison of responses. Figure 7 shows that for a range of different voltages and distances there is a linear relationship between mass deposition rate and electric current. More so, without requiring the intercept to be zero (no mass implies no current) the linear relationship gives an intercept nearly

zero with a fit only slightly better than one that forces an intercept with zero. Hence this relationship appears to make sense on the grounds of physical reasoning.

The linear relationship shown in Figure 7 indicates that there is a constant relating the flow of mass to the flow of charge. As the mass deposition rate has units of [kg/s] and the electric current has units of [C/s] this constant would have units of [kg/C]. The value for the data observed in Figure 7 is 96.1 C/kg. This is nearly an order of magnitude larger than that used for simulations by Kowalewski et. al. [13] and nearly two orders of magnitude larger than that used for simulations by Reneker et. al. [4]. As the charge on the fluid is the primary driving force for the electrospinning dynamics this is an important observation. It is possible that existing simulation work may not correspond to the physical situation of electrospinning PVOH.

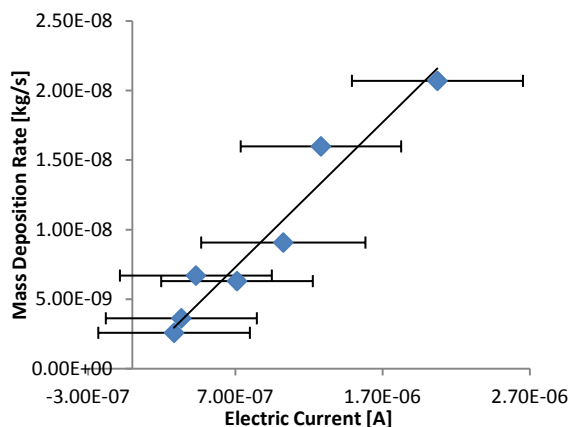


Figure 7: Mass deposition rate as a response to electric current drawn by the high voltage electrode for all combinations of voltage and distance studied in this work. The trend line is described by $m_{\text{rate}} = 0.01041 I$ ($R^2 = 0.938$). Vertical error bars representing the standard error obtained from the linear regression as presented in Table 1 are smaller than marker for each data point.

The constant charge density [C/kg] implies that there is a fixed quantity of charge regardless of electric field conditions or jet dynamics that must accumulate on the solution for electrospinning to occur. This may be related to the number of coulombs per square metre required to overcome the surface tension to form the Taylor cone or it may be related to the interaction between viscoelastic forces and the electrostatic forces drawing the jet. Regardless, the existence of a constant over a range of electrospinning conditions (applied voltage and electrode distance so a range of applied electric field strengths) is important to investigate. Discovering how this constant relates to other

parameters, if any, will help illuminate the fundamental mechanisms of electrospinning. Already, existing work indicates that the electric current drawn by either electrode can be, once properly characterized, used as a feedback signal to indicate the mass flow rate between the electrodes for any constant flow electrospinning process. This could allow further automation of the electrospinning process.

Conclusions

This work aimed to find a relationship between the mass deposition rate and the electric current for a range of electric field conditions produced by different applied voltages and electrode distances. This was done by measuring the increase in mass on the collector electrode and recording the electric current drawn from the high voltage power supply at different electrospinning conditions.

Previous research has observed a power law relationship between applied electric field and the mass deposition rate or electric current. The relationships described in this paper were found to be $m_{\text{rate}} \propto V^2$ where I is in [μA] and V is in [kV] while the deposition rate was

$m_{\text{rate}} \propto V$ where m_{rate} is in [kg/s] and V is in [kV]. Additionally the relationship between the mass deposition rate and electric current was found to be linear for a wide range applied electric field conditions. The linear relationship was found to be $m_{\text{rate}} = 0.01041 I$ where m_{rate} is in [kg/s] and I is in [A]. This gradient corresponds to a constant charge density of 96.1 C/kg for all combinations of applied voltage and electrode distance. It was found that the parallel plate approximation was not a valid estimation of the applied electric fields.

The constant charge density found was at least an order of magnitude larger than that typically used in simulations suggesting that a higher charge density may be required to describe the physical reality of electrospinning. Additionally the constant charge density means that the flow rate can be controlled automatically by using the electric current as a feedback signal for continuous flow electrospinning.

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