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Jonathan J Stanger

Nick Tucker

Kerry Kirwan

Stuart Coles

Daniel Jacobs, et al.

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Jonathan Stanger^{†‡}, Dr. Nick Tucker[‡], Dr. Kerry Kirwan[§], Dr. Stuart Coles[§], Dr. Daniel Jacobs[§], Dr. Mark P Staiger[†]

[†] Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch, 8041, New Zealand

[‡] Food and Biomaterials Group, Crop and Food Research Limited, Private Bag 4704, Lincoln, 7608, New Zealand

[§] International Manufacturing Research Centre, University of Warwick, Coventry, United Kingdom

Correspondence: jon@jonathanstanger.com

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Abstract

A detailed understanding of charge density and its origins during the electrospinning process is desirable for developing new electrospinnable polymer-solvent systems and ensuring mathematical models of the process are accurate. In this work, two different approaches were taken to alter the charge density in order to measure its effect on the Taylor cone, mass deposition rate and initial jet diameter. It was found that an increase in charge density results in a decrease in the mass deposition rate and initial jet diameter. A theory is proposed for this behaviour in that an increase in charge density leads to the tip of the Taylor cone forming a smaller radius of curvature resulting in the concentration of electric stresses at the tip. This leads to the electrostatic forces drawing the initial jet from a smaller effective area or “virtual orifice”.

Introduction

Electrospinning is a method of using high strength electric fields (>1 kV/cm) to draw a jet of polymer into fibres. It is difficult to predict the behavior of a new polymer in the electrospinning process in the absence of a complete model of the process. The most complete model to date does not incorporate the initial Taylor cone generation¹. The charge carried by the jet in this model is determined experimentally. None of the process models presented use the calculated charge based on the actually solution properties. The generally accepted charge carrier model assumes that the charge in the solution is generated by an imbalance of ions caused by ionic drift under the influence of the external electric field². This lack of process models that address the nature and generation of charge carriers is concerning as all the existing models

include either charge density or surface charge as a significant factor in the model¹⁻⁵.

In this work a series of ionic salts were added to an aqueous solution of poly(vinyl alcohol)(PVOH) before electrospinning the solution into fibres to determine if increasing the number of ions in solution would increase the charge carried by the solution and hence increase the mass of fibre generated. Past studies have shown that the addition of an ionic surfactant triethyl benzyl ammonium chloride to a solution of polyurethane dissolved in dimethyl formamide increases the fibre mass deposition rate⁶. However, it was unclear if the surfactant or increase in ions was responsible for increased fibre mass.

In this work, it was found that the addition of an ionic salt increases the charge density due to the increased concentration of ions, giving the

solution a higher conductivity, although this concurrently led to decreases in fibre deposition rates. This apparent anomaly is addressed by examining the effect of charge density on the Taylor cone and subsequent dimensions of the formed fluid jet.

Experimental procedure

Experimental materials

Electrospinning was carried out using poly(vinyl alcohol) (PVOH) (Chemiplas NZ limited, Wellington, NZ) with an average molecular weight of $118,000 \text{ gmol}^{-1}$ and a degree of hydrolysis (DH) in the range of 85-90%. The solvent used was water and the final concentration of PVOH for all experiments was 8% w/w.

The ionic salts used were lithium chloride (LiCl), lithium bromide (LiBr), lithium fluoride (LiF) and sodium chloride (NaCl). Assuming equivalent chemical conditions, the order of ionic radii for the cations is $\text{Na} > \text{Li}$, while for the anions the order is $\text{Cl} > \text{Br} > \text{F}$. This gave a range of different ionic radii, solubilities and molar conductivities (Table 1).

Ionic salt	Molar conductivity (mS/cm.mol)	Solubility
LiF	94.1	0.16g/100mL
LiBr	116.8	160g/100mL
LiCl	115.0	83.5g/100mL
NaCl	123.4	35.9g/100mL

Table 1: Properties of ionic salts used.

Electrospinning apparatus and analysis

All samples were electrospun at a potential difference of 7 kV and working distance of 10 cm (Model ES1, Electrospinz Ltd., New Zealand). Collector electrodes consisted of 150 mm square sheets of Al. Following 900 s of fibre deposition, samples were dried for 8 hr (RH 40%, 25°C) before weighing. Ionic salts were added incrementally to solutions and 3 samples were electrospun at each concentration step.

The fibre mass deposition rate was taken to be an average of 3 different measurements (Mettler Toledo AG204). The electrical current was measured as the maximum current observed after approximately 450 s of electrospinning (Metrix MX0056C multimeter, $\pm 10 \text{ nA}$). The multimeter was connected in series between the collector electrode and ground. The initial jet diameter was measured using a digital USB microscope (Model QX5, Digital Blue Corp., 60 \times). The

diameter of the jet was then measured using the image analysis software at a distance of 100 microns from the simulated surface of the droplet without the Taylor cone.

Results and Analysis

The conductivity of a solution takes into account both the ion size and concentration. As such all subsequent graphs are plotted against the conductivity of the solution as calculated by Eq. 1 where κ is the solution conductivity, Λ_0 is the molar conductivity of the ionic salt, c is the ionic salt concentration, A & B are constants derived from tabulated data and $\kappa_{8\% \text{ PVOH}}$ is the measured conductivity of 8% PVOH.

$$\kappa = \Lambda_0 c - (A + B\Lambda_0)c^{3/2} + \kappa_{8\% \text{ PVOH}} \quad (1)$$

The observed mass deposition rate (Fig. 2a) best fits an exponential function ($R^2 = 0.86$). This form was chosen over a linear model ($R^2 = 0.74$) because of the better fit and over a logarithmic model ($R^2 = 0.83$) because of the validity of the model at zero concentration. The exponential function has an asymptote indicating the lowest mass deposition rate is 0.0035 g/h. As salt concentrations above saturation have not been explored this model is invalid in this region. The trend in the mass deposition rate is the opposite of that observed by Ref. 6 where it is found that the addition of the ionic surfactant (triethyl benzyl ammonium chloride) increases the mass deposition rate. This may be due to the decrease in the surface tension that will change the shape of the Taylor cone and resultant jet. The ionic salts used in this work are not surfactants and since surface tension is important in electrospinning⁵, a different outcome has been observed.

The measured electric current is assumed to be the flow of charge incoming from the PVOH fibres impacting the collector electrode. As the conductivity increases the electrostatic current increases (Fig. 2b). Similarly, Ref. 6 reported an increase in the electric current with increasing salt concentration.

Charge density can be calculated using Eq. 2 where I is the electric current, m_{rate} the mass deposition rate and ρ the density of the solid polymer. The calculated quantity gives no indication of the position of the charge in the jet. As long as the assumptions of charge conservation and mass conservation hold true it is possible to use this equation to estimate the charge further up the jet. However considering

the equation is dependent on observations at the collector electrode; this being after the transition from a liquid solution to a solid fibre, it is only certain to be true for the moment of impact at the

collector. Hence only final charge density will be examined. As conductivity increases the charge density increases as observed in Fig. 3.

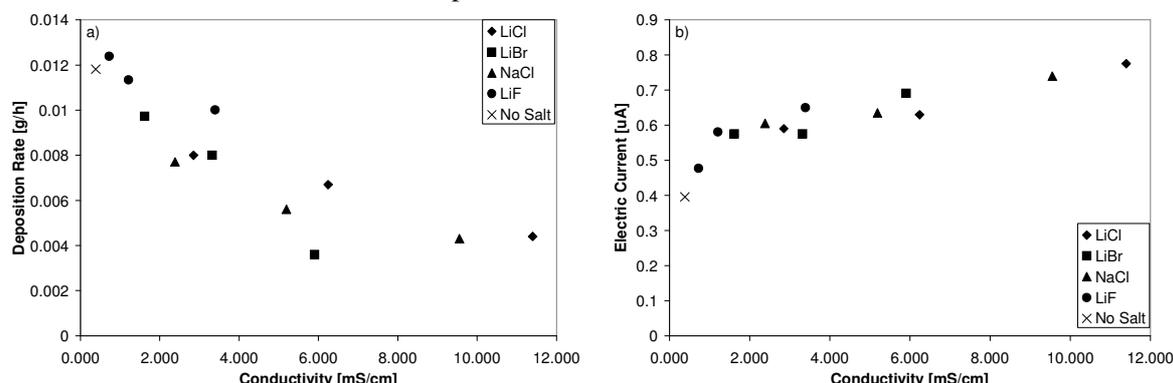


Fig. 2: (a) Average deposition rates as a function of conductivity ($m_{rate} = 0.0035 + 0.0099e^{-(0.254k)}$) (b) Observed effect of the addition of ionic salt on the electric current flowing to ground from the collector

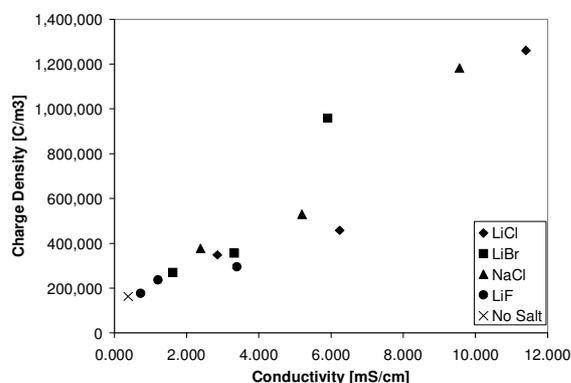


Fig. 3: Observed trend between final charge density and salt concentration.

A further investigation was undertaken to determine if there is any relationship between the initial jet diameter and deposition rate (Fig. 4) where the initial jet diameter has been modified by different combinations of ionic salt additions and charge polarity. Fitting a linear model to the data ($R^2 = 0.87$) showed a good fit. The model was forced to accept an intercept at zero as it makes no physical sense for a jet with zero initial diameter to be able to have a deposition rate.

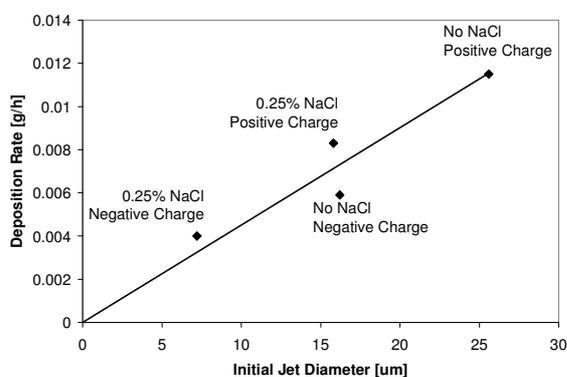


Fig. 4: Mass deposition rates linear dependence on the initial jet diameter. Linear model function of the form $m_{rate} = 0.0005d$. Note: Each point represents a single sample measured

$$\sigma_{density} = \frac{I\rho}{m_{rate}} \quad (2)$$

Discussion

Charge density as a function of ion concentration

With an increase in conductivity there is a corresponding increase in the observed charge density (Fig. 2b). This fits with the generally accepted model of charge carrier generation where ions of the opposite charge to the electrode in the solution are neutralized leaving an excess of ions of the same charge as the electrode². It was shown by Ref. 5 that by calculating the characteristic charge and hydrodynamic relaxation times for the solution at the electrode that the solution behaves as a conductor. Using this assumption and the above mentioned charge carrier generation mechanism it is possible to form an equation (Eq. 3) for the rate of charge transfer (electric current). Here I is the total electric current flowing in the jet, k the conductivity of the solution, E the electric field strength and r the radius of the jet.

$$I = kE\pi r^2 \quad (3)$$

The generation of charge in the solution is dependant on the conductivity of the solution which is directly related to the ion concentration. Having established already that the charge density is dependant on the current in the jet (Eq. 2) the connection between the increase in charge density and ion concentration has been established in terms of a physical process. Hence the assumption will be made that the increase in charge density is due to the increase in the ion concentration.

Mass Transport when Charge Density is Increased

Taylor cone formation is due to the accumulation of charge in the fluid and the resultant competition between surface tension and surface charge repulsion⁵. Therefore, it is expected that an increase in charge density in an electrospinning fluid should influence the resultant behavior of the fluid droplet.

The droplet evolution moves towards a cone shape with a sharp radius of curvature at the tip, representing a supercritical state⁵. The jet evolution is likely to be driven by the concentration of electric stresses at the tip due to the small radius of curvature. The authors are not aware of any investigation of how the shape of the Taylor cone changes due to different values of charge density. Experimental observations (Fig. 3 and Fig. 4) suggest that as the charge density increases the cone will adopt a steeper angle with a smaller radius of curvature at the tip.

With a smaller radius of curvature at the tip of the cone there will be a smaller cross section with a high charge density that the electrostatic field will act on to form a fluid jet. This could be visualized as a “virtual orifice” through which the jet is formed (see Fig. 5). If this is true the result will be that a smaller jet will be evolved when the radius of curvature is decreased. It has been observed that when the charge polarity applied to an aqueous solution of PVOH is negative the charge density increases, decreasing the initial jet diameter and resulting deposition rate when compared to a positive polarity⁷. Combining these observations with those from Fig. 3 and Fig. 4 shows that when there is a higher charge density the initial jet diameter decreases. This supports the theory that increasing the charge density results in a smaller radius of curvature which in turn results in a thinner initial jet.

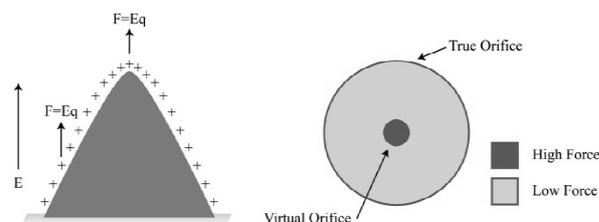


Fig. 5: Charge concentration at the tip produces a virtual orifice.

The trends shown in Fig. 2a and Fig. 3 show that with an increase in charge density there is a corresponding decrease in total mass transported between the two electrodes (mass deposition rate). This matches with the observed trend when the sign of the charge is reversed⁷, where the increase in charge density is not due to an increase in ion concentration. A linear relationship between initial jet diameter and deposition rate was observed since the Taylor cone is formed as the balance between the forces of surface tension, electrostatic repulsion at the surface and internal fluid pressure (Fig. 4). When charge density increases the electrostatic forces become stronger leading to a steeper cone and subsequently a narrower initial jet.

Conclusions

- Increasing ion concentration leads to increased charge density in the electrospinning jet (i.e. more charge carriers) as expected;
- An increase in charge density by addition of ionic salt or changing the charge polarity of the solution results in a narrower initial jet and less mass transported;
- A “virtual orifice” model is proposed to explain decreased mass deposition from the tip of the Taylor cone. When charge density increases the cone becomes steeper and the virtual orifice becomes smaller.

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