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Jonathan J Stanger
Nick Tucker
Mark P Staiger
Kerry Kirwan
Stuart Coles, et al.

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

[†] 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

Fibres with a diameter in the nanometer range were electrospun from aqueous poly(vinyl alcohol) (PVOH). In order to improve the mass deposition rate and decrease the final fibre diameter salts (NaCl, LiCl, LiBr and LiF) were added to the solution. The aim was to increase the charge density and hence increase the electrostatic forces on the fluid. It was found that with increasing salt concentration the charge density did increase. However the mass deposition rate was found to decrease and the final fibre diameter was found to increase. The decrease in mass deposition rate is explained by considering the concept of a virtual orifice. The increase in the final fibre diameter is explained by considering the charge distribution in the jet when it behaves like a conductor compared to when it behaves like an insulator. Both mechanisms result from the increase in conductivity of the PVOH solution without significantly modifying other solution properties when salt is added.

Introduction

Electrospinning is a method of using high strength electric fields (>1 kV/cm) to draw a jet of polymer into nanometre diameter fibres¹. The application of high voltage causes the droplet formed at the tip of the electrospinning head to become charged. This charge then causes the droplet to form a cone (Taylor cone) and eject mass in the form of a fluid jet². Further down the jet an instability forms that causes the jet to whip around and thin down to nanometre scale diameters³. The force that drives this instability is proportional to the surface charge on the jet squared⁴. As such this work aims to explore the addition of a salt to the electrospinning solution

in order to draw more mass from the Taylor cone and to increase the force of the bending instability to result in a larger mass of thinner fibres.

There has been little work done on the general principle of using additives to modify the conductivity of the polymer solution. Some work has shown that an increase in conductivity would result in an increase in the fibre diameter⁵⁻⁸. In a number of other papers the effect of conductivity has been proposed to cause a decrease in the fibre diameter⁹⁻¹⁵. Only the work by^{6-8, 10} deal with salts that have neutral pH. In the other papers solution properties other than

conductivity also change which may account for the lack of consensus in literature.

In the present work, a series of different salts were added to an aqueous solution of poly(vinyl alcohol)(PVOH) and electrospun. The aim is improve the process for industrial applications by increasing the mass transfer rate and decreasing the final fibre diameter as a result of increasing the number of ions in solution. The mass deposition rate, average fibre diameter and electric current flowing to the collector to neutralize the charge on the incoming fibres were all measured as a function of the salt concentration. From these three variables charge density in the fibre as it impacts with the collector can be calculated. It was found that with increasing ion concentration the charge density did increase as expected. However it was found that this did not result in more mass of fibres being deposited nor the fibre diameter decreasing. Examining how an increase in charge density affects the Taylor cone shape explains the lower mass deposition rate. Examining how the change in conductivity affects the way charge is distributed in the jet explains the thicker final fibre diameter.

Experimental

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).

Salt	Molar conductivity (mS/cm.mol)	Solubility	Concentration steps (wt.%) ^a
LiF	94.1	0.16g/100mL	0.01, 0.025, 0.1
LiBr	116.8	160g/100mL	0.1, 0.25, 0.5
LiCl	115.0	83.5g/100mL	0.1, 0.25, 0.5
NaCl	123.4	35.9g/100mL	0.1, 0.25, 0.5

Table 1: Properties of ionic salts used. ^awt.% relative to the total solution weight

Electrospinning apparatus and analysis

All samples were electrospun at a potential difference of 7 kV and working distance of 100 mm (Model ES4, Electrospinz Ltd., New Zealand). The pressure of the polymer solution at the spinning head (varied by a gravity feed system) was used as the control variable. Once stable spinning was attained the pressure was kept constant. Cleaned, nominally 150 mm per side square sheets of aluminium were used as the collector electrode. Following 900 s of fibre deposition, samples were dried for 8 hr (RH 40%, 25°C) before weighing. Salts were added incrementally to solutions and 3 samples were electrospun at each concentration step (Table 1).

The fibre mass deposition rate was taken to be an average of 3 different samples (Mettler Toledo AG204). The electrical current was measured as the constant 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 exact position for measurement of the initial jet diameter was determined systematically by visualizing the Taylor cone as a droplet and then measuring the jet diameter 100 μm from the extrapolated perimeter of the droplet (see Figure 1). This allows the measurement to be made in the same place regardless of different conditions. The "initial" jet diameter was measured using images from a digital USB microscope (Model QX5, Digital Blue Corp., 60 \times). The final fibre diameter was measured using images from a scanning electron microscope (JEOL 7000F FE-SEM JEOL Ltd., Japan). UTHSCSA ImageTools software was then used for all image analysis.

Results

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 using a modified Debye-Huckel-Onsager equation (Equation 1) where κ is the solution conductivity, Λ_0 the molar conductivity of the salt, c the salt concentration, A and B are constants derived from tabulated data, and $\kappa_{8\% \text{ PVOH}}$ the measured conductivity of an 8 wt.% PVOH aqueous solution.

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

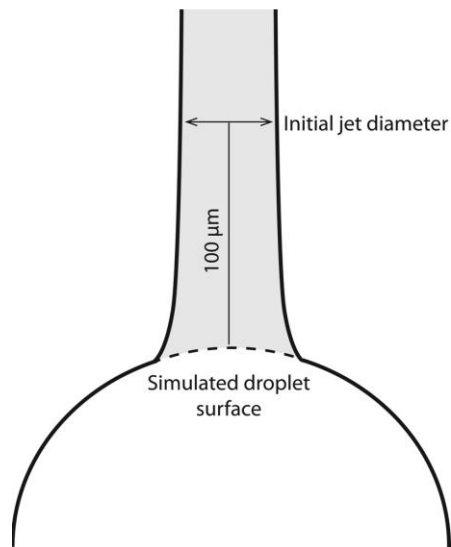


Figure 1: Systematic procedure for measurement of the initial jet diameter.

It has been shown in literature that initially the polymer solution can be considered to be a conductor². As such with an increase in solution conductivity there is the expected increase in the

measured electric current flowing to ground from the collector (Figure 2).

It is observed that with an increase in conductivity there was a corresponding decrease in the mass deposition rate (Figure 3). The trend in the mass deposition rate is the opposite to that observed by⁵ 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 changes the shape of the Taylor cone and resultant jet. The salts used in this work are not surfactants and since surface tension is important in electrospinning², a different outcome has been observed.

Comparison of the initial jet diameter between PVOH with no salt and with 0.25% NaCl shows a decrease from 61 μm to 42 μm . As there is a corresponding decrease in the initial jet diameter and in the mass deposition rate this will be due to a change in the size of the “virtual orifice”¹⁷.

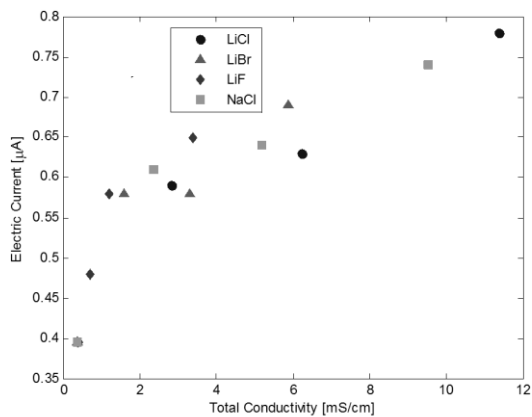


FIGURE 2. Observed effect of the addition of salt on the electric current flowing to ground from the collector.

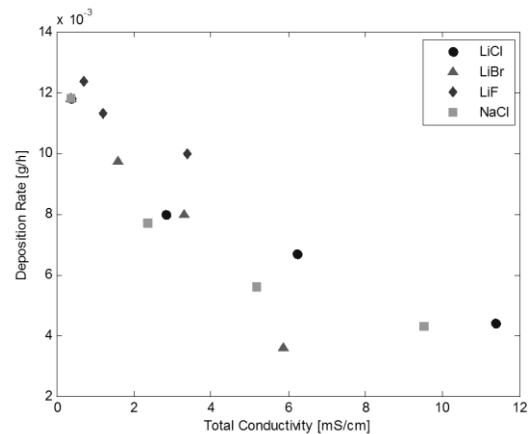


FIGURE 3. Observed average deposition rates as a function of conductivity.

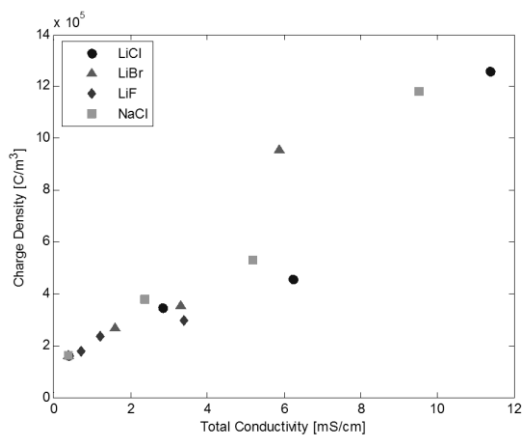


Figure 4. Observed effect of the addition of salt on charge density in the fibre when impacting with the collector.

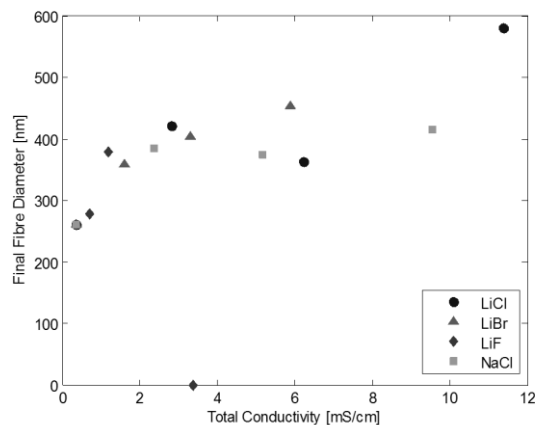


Figure 5. Observed average fibre diameter as conductivity increases (average of over 300 measurements per sample).

The final charge carried by the jet as it impacts with the collector can be calculated using Equation 2. It can then be demonstrated that the increase in conductivity results in a higher charge density (Figure 4). With an increase in conductivity it was also found that there was an increase in fibre diameter (Figure 5). As the force that drives the whipping instability is proportional to the square of the surface charge⁴ it is unexpected that the increased charge carried by the jet results in a thicker fibre. It is possible that the final fibre diameter reaches a constant value of approximately 400nm for all conductivity values above approximately 3 mS/cm. This may indicate that the expected effect of an increase in charge density may reach an equilibrium with another counter effect.

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

The trend of increasing fibre diameter due to salt addition is the same as observed by some authors⁵⁻⁸ but differs to the trend observed by others⁹⁻¹⁵. In the case of^{9, 10} they used ionic surfactants which would cause additional effects that could account for the different observed trend.^{11, 14} used a polyelectrolyte to increase conductivity and hence would also change the initial solution properties. Other work by^{12, 13} involved the change of pH of the solution which was also shown to change the initial solution properties. The work by¹⁵ was the most directly comparable result, using 0.05% NaCl with PVOH to decrease the diameter from 214 nm ± 19nm to 190nm ± 19nm. This puts the decrease within the limits of error. The results obtained by⁶⁻⁸ all resulted from the use of pH neutral non-surfactant salts. In each case more than one salt was used and all salts resulted in higher final fibre diameter.

Discussion

It has already been shown the addition of a salt to a solution of PVOH results in an increase in both the electric current flowing to ground from the collector and the charge density in the fibre. However it was unexpected that this would result in a decrease in the mass deposition rate and the final fibre diameter. The concept of the “virtual orifice” can be used to explain the decrease in the mass deposition rate. The increase in the fibre diameter can be explained by considering the mode of charge transport in the jet and how this changes over the flight of the fibre.

As outlined in another paper¹⁷ the “virtual orifice” is a way of considering how an increase in the charge on the polymer solution will effect the shape of the Taylor cone. With no charge a droplet would form a hemi-spherical shape. An increase in the charge density results in an increase in the electric field driven distortion that push the droplet into a more conical shape. Hence the increase in charge density would result in the Taylor cone adopting a sharper “point” to the cone which would translate to a thinner initial jet being ejected from the tip of the cone. With a thinner jet there is a smaller “virtual orifice” that the viscous polymer solution must be squeezed through. This limits the flow of polymer solution at a given pressure which limits the mass of fibre that can be deposited.

The initial mode of charge transfer is that of an ohmic nature.² showed this to be the case by comparing the relaxation time constant for the electric charge and the hydrodynamic fluid and found that the charge is able to redistribute significantly faster than the fluid (conductive behaviour) in a typical case. However it was also found that once the fibre was in flight the fluid reached a velocity such that the hydrodynamic relaxation time became smaller than the charge relaxation time (insulator behaviour). This becomes important when we consider how the charge is distributed in conductors and insulators. In a conductor the charge will have some cross sectional distribution but in an insulator the charge will be entirely concentrated at the surface. It has been shown that the force driving the bending instability and hence fibre thinning, is directly proportional to the square of the surface charge. If the transition to insulator behaviour was delayed then the final fibre diameter would increase. The charge relaxation time varies proportional to inverse conductivity so the increase in conductivity gives a faster relaxation time. All else being constant this would delay the transition to insulator behaviour by requiring a higher fibre velocity to be reached. This mechanism fits well to account for the counter effect mentioned in the results section. The delay in charge migration explains why an increase in conductivity can result in thicker fibres, by decreasing the initial force in the bending instability. As mentioned in the results section if the decrease in initial force on the fibre caused by the delay in charge migration is offset by the increased force once all the charge has migrated then the fibre diameter would become

approximately constant with increasing conductivity.

Conclusion

Adding salt does increase the charge density in the polymer solution. It has been shown that the decrease in the mass deposition rate was caused by the increase in charge density. More charge leads to higher electrical distortion of the droplet shape, forming a thinner jet. This thinner jet then restricts the viscous flow of polymer solution when a constant pressure supply is used. Additionally the addition of salt raises the conductivity of the polymer solution giving a shorter charge relaxation time. This means that the transition between conductor and insulator behavior takes longer. This has the effect of delaying the gathering of charge on the surface of the fibre. Hence a decrease in the force driving fibre thinning and the production of thicker fibre. As such this technique doesn't increase the mass production or reduce the fibre diameter and hence may not be industrially useful. However if the conductivity is too low the increase in conductivity can allow electrospinning to start.

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References

1. J. Doshi and D. H. Reneker, *Journal of Electrostatics* **35**, 151-160 (1995).
2. S. N. Reznik, A. L. Yarin, A. Theron and E. Zussman, *Journal of Fluid Mechanics* **516**, 349-377 (2004).
3. D. H. Reneker, A. L. Yarin, H. Fong and S. Koombhongse, *Journal of Applied Physics* **87** (9), 4531-4547 (2000).
4. A. L. Yarin, S. Koombhongse and D. H. Reneker, *Journal of Applied Physics* **89** (5), 3018-3026 (2001).
5. M. M. Demir, I. Yilgor, E. Yilgor and B. Erman, *Polymer* **43** (11), 3303-3309 (2002).
6. C. Mit-uppatham, M. Nithitanakul and P. Supaphol, *Macromol. Chem. Phys.* **205**, 2327-2338 (2004).
7. X.-H. Qin, E.-L. Yang, N. Li and S.-Y. Wang, *Journal of Applied Polymer Science* **103**, 3865-3870 (2007).
8. X. Zong, K. Kim, D. Fang, S. Ran, B. S. Hsiao and B. Chu, *Polymer* **43** (16), 4403-4412 (2002).
9. J. S. Choi, S. W. Lee, L. Jeong, S.-H. Bae, B. C. Min, J. H. Youk and W. H. Park, *International Journal of Biological Macromolecules* **34**, 249-256 (2004).
10. J. Zeng, X. Xu, X. Chen, Q. Liang, X. Bian, L. Yang and X. Jing, *Journal of Controlled Release* **92**, 227-231 (2003).
11. M. Li, Y. Guo, Y. Wei, A. G. MacDiarmid and P. I. Lelkes, *Biomaterials* **27**, 2705-2715 (2006).
12. W. K. Son, J. Ho Youk, T. Seung Lee and W. H. Park, *Materials Letters* **59** (12), 1571-1575 (2005).
13. W. K. Son, J. H. Youk, T. S. Lee and W. H. Park, *Journal of Polymer Science: Part B: Polymer Physics* **42**, 5-11 (2004).
14. W. K. Son, J. H. Youk, T. S. Lee and W. H. Park, *Polymer* **45**, 2959-2966 (2004).
15. C. Zhang, X. Yuan, L. Wu, Y. Han and J. Sheng, *European Polymer Journal* **41**, 423-432 (2005).
16. CRC-Press, *CRC Handbook of Chemistry and Physics*, 84 ed. (CRC Press, Cleveland, Ohio, 2004).
17. J. Stanger, M. P. Staiger, N. Tucker and K. Kirwan, *Solid State Phenomena* **151**, 54-59 (2009).