Hot electrospinning of polyurethane fibres

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ABSTRACT

Several polyurethane solutions of the same composition but varying temperature (25, 50, 75 and 100 °C), were subjected to an electric field whilst flowing through a conducting nozzle. All other typical electrospinning parameters (applied voltage, medium infusion rate and collecting distance) were kept constant. The effects of processing solution temperature on the resulting fibre morphologies were assessed using optical and scanning electron microscopy, and were also correlated with solution properties (surface tension, viscosity, electrical conductivity and density). It was observed that increasing the solution temperature leads to a significant reduction in the mean diameter and size distribution of the resulting fibres. Increasing the temperature from 25 to 100 °C enabled the reduction of the mean fibre diameter from 2.5 μm to 1.2 μm. The T_m value of resulting fibres generally increased as the solution processing temperature increased suggesting a change to the orientation of polymer chains in the overall structure.

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1. Introduction

The electrospinning or electrospraying process is a simple manufacturing technique which utilises electrostatic forces exerted on a drop ejected from the tip of a needle under the influence of a high electrical potential difference. The utilisation of this process has expanded in the last decade largely due to an increasing interest in micro and nano technologies, especially involving polymeric materials. In addition to producing structures in this size range, the process has the potential for high fibre output production. Other desirable features of the fabricated structures include high surface area to volume ratio and excellent mechanical properties, which have generated a considerable amount of interest from industry [1–3].

The electrospinning process may be broken down into several sub-processes. These can be classified as: jet-formation, jet-thinning in the presence of an electric field, formation of jet-instabilities and finally solidification and production of fibres [4,5]. The first part of the spinning process consists of charging a droplet of a polymer solution. The mode in which the liquid droplet exits the capillary is governed predominantly by the two main operating parameters -potential difference and the flow rate. The range of modes has been identified previously [6], and may also be sub-divided into two main groups: dripping and spraying. The first group consists of modes where the jet breaks up into small liquid fragments i.e. droplets. The second group consists of modes where the liquid is ejected from the capillary in the form of a jet which later disintegrates into charged droplets or the spinning process.

In electrospinning the fibre characteristics are determined by the processing parameters and can be tailored for numerous applications requiring different fibre morphologies and sizes (from nano- to micrometre). These include tissue engineering matrices (e.g. scaffolds for bone and soft tissue regeneration), textile engineering (including drug loaded wound dressings), drug delivery, filters, catalytic nanofibres and sensors [7–12].

The aim of this study is to determine the effectiveness of an additional control parameter on electrospun fibre characteristics by varying the processing solution temperature. Instabilities present during the electrospinning process may arise from the solution properties and/or operating conditions [13,14], therefore these will invariably regulate the morphology of resultant fibres. In particular, variation in fibre diameter has been attributed to the balance between stresses in the liquid (due to surface tension and electrostatic surface charge) vapour pressure, evaporation rate of the driving solvent and concentration of the solution [15,16]. Hence, altering the temperature of processing solutions will not only affect solution properties before fabrication (viscosity, surface tension, electrical conductivity etc.) but will also have an influence on solvent behaviour immediately after material emission from the electrospinning nozzle (evaporation, vapour pressure and polymer concentration). For instance, an increase in temperature will cause a decrease in the viscosity and surface tension whilst increasing the electrical conductivity and the vapour pressure of the solution. These factors are all crucial in determining the final fibre morphology therefore it is vital to correlate changes in temperature with the morphology of electrospun fibres [16–19].

2. Experimental procedure

Dimethyl-formamide (DMF) and Polyurethane (PU) (Poly [4,4′-methylenebis(phenyl-isocyanate)-*alt*-1,4-butanediol/polytetrahydrofuran) elastomer were purchased from Sigma-Aldrich (Poole,

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Table 1
Solution properties and the resultant mean fibre diameter and standard deviation at each solution processing temperatures (25, 50, 75 and 100 °C).

Processing solution	Solution temperature before and after processing (°C)	Surface tension mN m^{-1}	Viscosity mPa s	Electrical conductivity μs m^{-1}	Density Kg m^{-3}	Mean fibre diameter μm	Standard deviation
25	25,23	50	713	1.1	950	2.47	0.79
50	50,47	43	445	1.7	940	2.24	0.78
75	75,71	38	299	2.9	880	1.99	0.66
100	100,93	31	275	3.3	880	1.19	0.29

UK). A 10 wt% PU solution was prepared by mechanically stirring the polymer in DMF solution for 72 hours at the ambient temperature (20 °C). Once dissolved, the concentration of the solution was kept constant throughout experimentation by sealing the PU solution vial. The solution was then gradually heated to 100 °C and various characterisations (surface tension, electrical conductivity, viscosity and density) of

the polymer solution were performed at selected temperatures (25, 50, 75 and 100 °C) in a fume hood. The density of the solution was estimated using a standard 25 ml density bottle (VWR, Lutterworth, UK). Surface tension was measured using a KrÜss Tensiometer K9 (Krüs GmbH, Hamburg, Germany). Viscosity was measured using a Ubbelohde viskosimeter (Schott Instruments GmbH, Germany). Electrical conductivity was
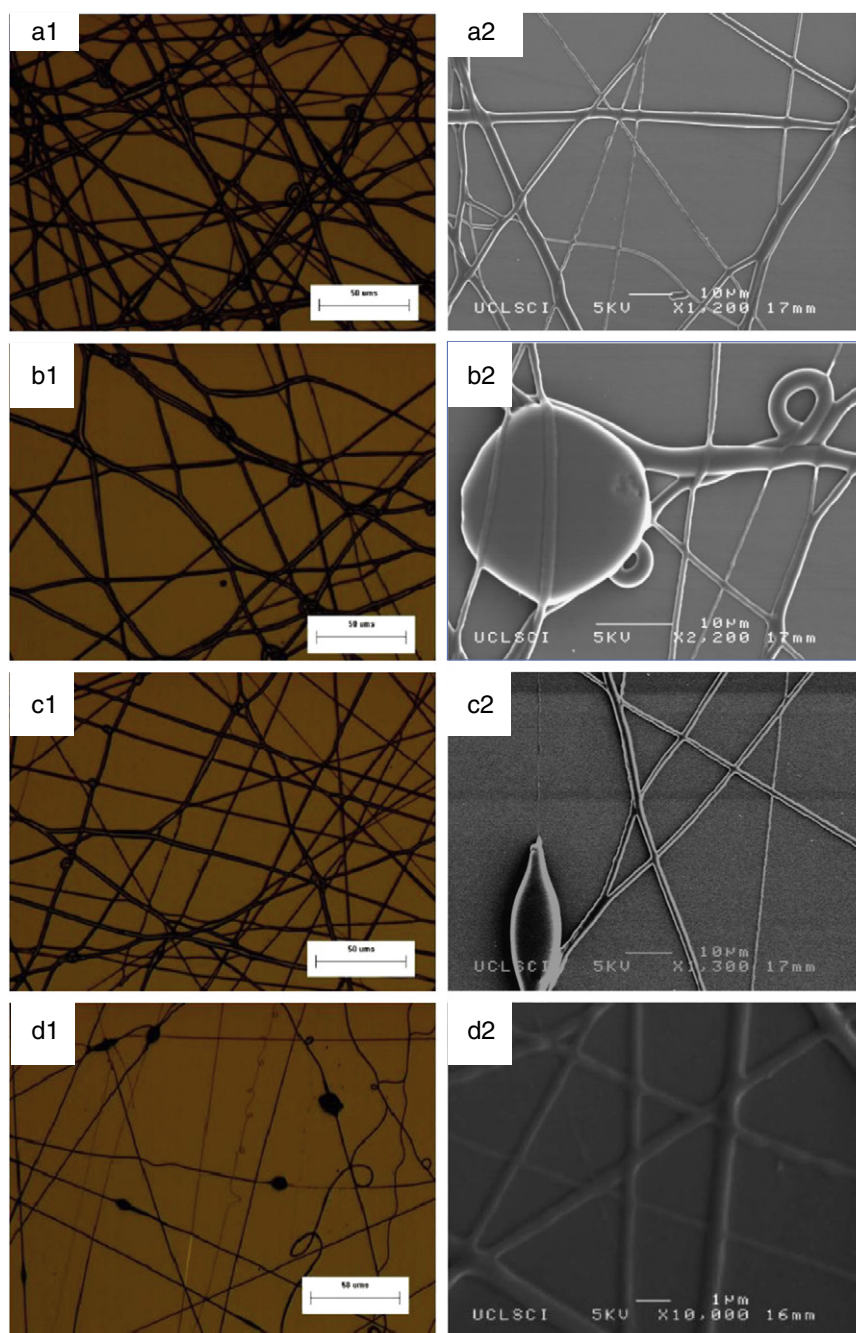

Fig. 1. Optical and scanning electron micrographs (respectively) of formed fibres using selected processing solution temperatures of (a1-a2) 25 °C (b1-b2) 50 °C (c1-c2) 75 °C and (d1-d2) 100 °C. [Applied voltage = 10 kV, Flow rate = 60 μl/min, Collecting distance = 100 mm and Collecting time = 20s]. [Scale bars for a1,b1,c1,d1 = 50 μm].

assessed using a HACH SensION ™ 156 probe (Camlab Ltd., Cambridge, UK). The temperature of the solution was recorded prior to and after measurements were obtained.

A second identical stock solution of PU solution was prepared in similar fashion and heated again gradually to 100 °C. The polymer solution was electrospun at previously allocated temperatures (25, 50, 75 and 100 °C), using minimal perfusion distances to prevent or minimise heat loss due to solution movement from the infuser to the processing nozzle. The set-up utilised comprised typical electrospinning components and a stainless steel needle with an inner orifice diameter of 480 μm was selected. The needle was coupled to a high voltage supply (Glassman Europe Limited, Tadley, UK), in an epoxy resin mould. PU solution was perfused through the needle at a controlled flow rate using a specially designed Harvard syringe pump (Harvard Apparatus Ltd., Edenbridge, UK). The operating parameters were fixed as: applied voltage 10 kV, flow rate 60 μl/min, collection distance 100 mm and collection time 20 seconds. A high speed camera (Weinberger AG, Dietikon, Switzerland) was connected to a computer, allowing the observation of the medium behaviour at the tip of the processing nozzle during the electrospinning process. Fibres were deposited on glass slides directly below the processing nozzle. After samples had been obtained, the temperature of the solutions was recorded immediately. Fibres were analysed using optical and scanning electron microscopes (SEM) (Nikon ME 600 and JEOL JSM 3600). For SEM analysis, samples were coated with a thin layer of gold. Samples were also analysed using Differential-Scanning Calorimetry (DSC) (Netzsch-Gerätebau GmbH, Wittelsbacherstr, Bavaria) at a temperature range between 20-400 °C, applying a heating step rate of 10 °C min^{-1}. This was used to determine the melting temperature (T_m).

3. Results and discussion

Controlled variations in processing solution temperature are expected to have an impact on the resultant electrospun structures. This can be due to changes in solvent drying properties once droplets or threads have been ejected from the processing nozzle. However, it is also important to characterise the physical properties of such solutions (i.e. electrical conductivity and viscosity) as these are well established aspects which can drive or hinder such processes. These measurements are shown in Table 1. All solutions were initially heated to 100 °C and were subjected to brisk mechanical stirring. This was to ensure that all solutions were homogeneous, thus reducing the effect of any internal thermal gradients and any external polymeric factors affecting solution properties, although the PU used in this work has a melting point much greater (>200 °C) than the highest temperature selected for solution processing.

The heat induced change to polymeric chains dictates the relationship between the viscosity and the temperature and is recognised as exponential. As the temperature is increased, the polymer chains in the liquid gain kinetic energy. This allows them to overcome the intermolecular forces of attraction which in turn decrease the cohesive forces. Therefore, a decrease in viscosity in liquids is observed as the temperature is increased. Surface tension, likewise, decreases as the temperature increases. Surface tension in its simplest form is the measure of the force per unit length along a line parallel to the surface of a material. This is caused by the cohesion of like molecules at the surface. As noted for the viscosity, the kinetic energy will increase with temperature causing a decrease in the molecular interaction of the molecules at the surface causing a decrease in surface tension. A decrease in both the viscosity and surface tension of the polymer solution causes a decrease in the visco-elastic nature of the fluid. Due to this, the Coulombic force of repulsion becomes the dominant effect present during electrospinning. The electrical conductivity as expected increased with temperature. The density of the solution showed no significant decrease from the lower to the upper limit of the two temperatures ranges (25, 50, 75 and 100 °C). There were minimal changes to the individual solution temperature in between the relevant characterisation steps.

The mean fibre diameter (Table 1) was seen to decrease as the processing temperature was increased, e.g. the reduction between 25 to 50 °C was 0.25 μm whilst from 75 to 100 °C it was 0.8 μm. The standard deviation in the fibre diameter measurements followed a similar pattern to the mean diameter. There was an insignificant decrease in the standard deviation between the lowest temperatures, as the temperature was increased, however, at the upper limit the standard deviation dropped rapidly.

Fig. 1 shows optical and electron micrographs of fibres produced using the various processing solutions, which visually demonstrate these changes. For example, fibres prepared from the 25 °C solution (Fig. 1**a1-a2**) were considerably coarser than those prepared from the 100 °C solution (Fig. 1**d1-d2**). Another phenomenon observed is the beading
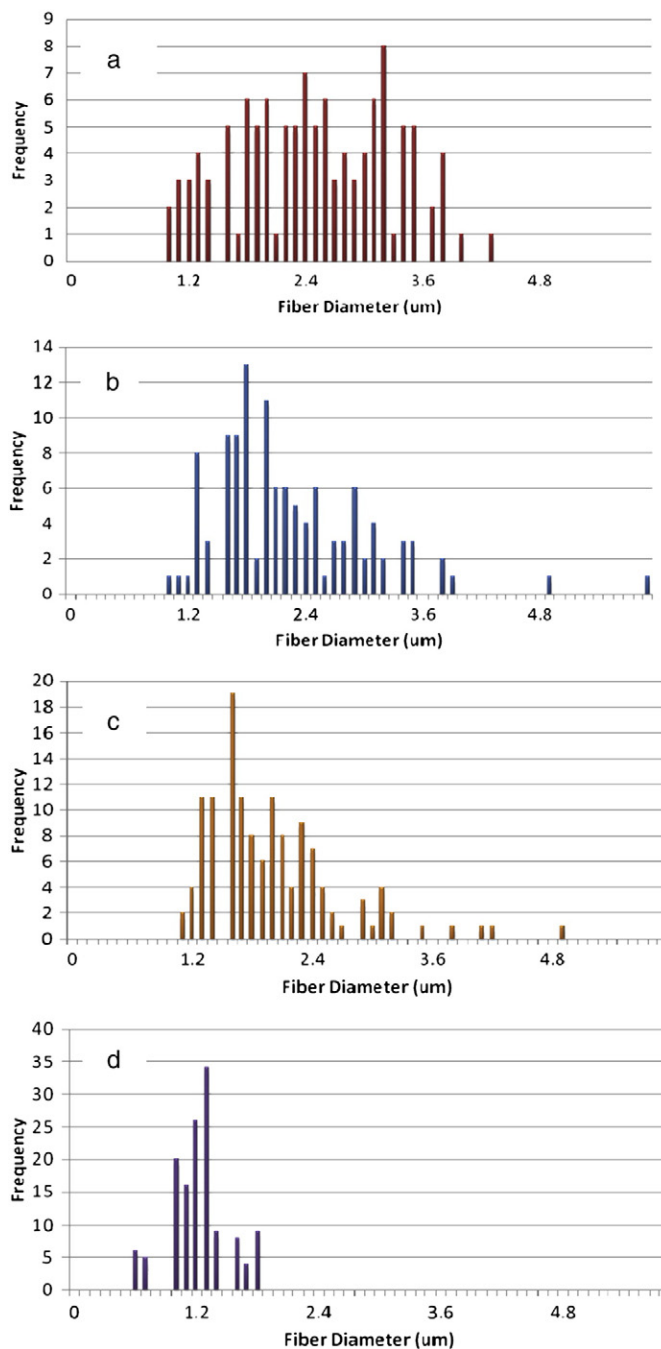
Fig. 2. Electrospun fibre diameter distribution obtained using selected processing solution temperatures of (a) 25 °C (b) 50 °C (c) 75 °C and (d) 100 °C.

variation in the fibres. At the lowest temperature the beads formed were more spherical and little transformation was seen from 25 °C to 50 °C. As the temperature was increased from 50 °C to 75 °C, the beads became elongated at the edges forming a spindle-like shape at the highest temperatures (Fig. 1c2).

The decrease in the mean fibre diameter may be attributed to both the reduction in surface tension and viscosity, in addition to the rise in the electrical conductivity. Additionally, changes to polymeric molecules resulting from a reduction in chain entanglements may also play a role in this reduction [20,21]. This in coalition with the decrease in viscosity and surface tension causes the viscoelastic relaxation time to drop significantly affecting the magnitude of the viscoelastic forces. Coulombic repulsion forces are thus dominant causing rapid elongation of the jet. Consequently, this allows the diameter of the fibres produced to decrease significantly [1,16].

The rate of evaporation and the vapour pressure of the solution decrease significantly as the processing solution temperature drops. Therefore, at the lowest temperatures, the solidification time of the solution is greatest, allowing additional elongation of the jet. Due to the solidification, the solvent has evaporated to such an extent that the intermolecular forces between the polymer molecules oppose further stretching of the liquid. A "terminal" diameter for the fibres is thus reached.

Analysing the fibre diameter size distribution resulting from the various processing solutions (Fig. 2) reveals a clear trend. The distribution of fibres obtained using the 25 °C solution (Fig. 2**a**), shows a broad range of fibre production from 0.9-4.3 μm, with a bell shaped population distribution in between these values. However, increasing the solution temperature to 50 °C, results in a skew towards the lower limit of 0.9 μm (Fig. 2**b**), although some outliers appear beyond the initial upper limit of 4.3 μm. Increasing the processing solution temperature further to 75 °C (Fig. 2**c**), further slants the distribution towards the lower limit. However, once a processing solution temperature of 100 °C is utilised (Fig. 2**d**), finer fibres (0.5 μm) are formed in addition to a much more uniform distribution, skewed around the initial lower limit. Hence the use of heat can be applied to refine fibre distribution, giving rise to a much more uniform population. There is also potential to reduce fibre sizes using heat- assisted spinning.

The spun fibres were analysed using DSC as shown in Fig. 3. Even though the various polymer samples were prepared from the same PU concentration solution, which were all subjected to 100 °C, there is a clear difference in the melting endotherm values. PUs are segmented and can demonstrate different degrees of crystallinity according to the processing conditions [22]. Furthermore, without the addition of heat, parametric variations in the electrospinning process (e.g. applied voltage, infusion rate) can also alter the melting temperatures of fibres prepared from the same solution [23].
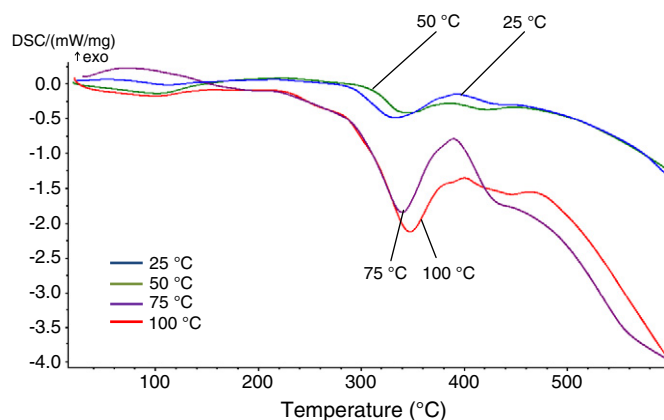
It may be seen that as the processing solution temperature was increased there was an increase in the T_m. For example, fibres prepared using the 100 °C solution had a T_m of 347 °C, which is higher than the values obtained when processing solutions at lower temperatures (e.g. T_m for 75, 50 and 25 °C were 339, 338 and 333 °C, respectively). It is also clear that as the processing temperature is increased the enthalpy of fusion also increases, although there is some overlap between fibres prepared from 25 and 50 °C solutions (area is increased due to broader peaks). It has been shown previously that the level of crystallinity is increased when using the electrospinning process, going from film to fibre morphology, resulting in an increase in the T_m values. In relation to our findings, heat assisted electrospinning favours this structural enhancement further as there is an increment in the T_m, at elevated temperatures, arising from the formation of domains (in fibres) due to increased movement of polymeric chains yielding greater crystallinity [24].

4. Conclusions

In this work, PU fibres were produced using typical electrospinning apparatus. The role of temperature on the final morphology of the fibres was investigated by optical and scanning electron microscopy. Key solution properties were measured in order to correlate the effect of the solution temperature on the final fibre morphology. It was found that heat assisted electrospinning of PU fibres can be used to refine the diameter distribution of PU fibres generated in a spinning operation. Beading is also altered when the solution temperature is varied, going from spherical to needle shaped morphologies. Finally, as PU crystallinity can be varied using various material processes requiring heat, controlling the temperature of PU solutions during electrospinning can lead to variations in T_m arising from changes in the orientations (and segmentation) of PU polymeric chains.

Acknowledgments

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Fig. 3. DSC curves of fibres formed at selected processing solution temperatures (25, 50, 75 and 100 °C).