IOP Conference Series: Materials Science and Engineering

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To cite this article: Ainaa Amirah Md Zubir *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **778** 012087

IOP Conf. Series: Materials Science and Engineering **778** (2020) 012087 doi:10.1088/1757-899X/778/1/012087

Electrospinning of PLA with DMF: Effect of polymer concentration on the bead diameter of the electrospun fibre

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Abstract. Electrospinning has been known for its' ability in producing nanoporous fibres which uses electrical force to form a spinning jet out of a polymer solution. The electrospinning condition and polymer solution properties can influence the electrospinning jet formation as well as jet path. Polylactic acid (PLA) was dissolved in dimethylformamide (DMF) to produce a polymer solution. Bead is considered as a defect towards an electrospun fibres, yet previous study found that PLA/DMF produced beaded fibres for all concentrations. However, there is a limited study that explain the effect of concentration on the diameter of beads. Therefore, in this study we investigated the formation of electrospinning jet as well as the effect of PLA concentration of formation of beads, particularly the diameter of the beads. Polymer solution with different concentration was prepared. The concentration investigated in this study were 7.5, 10, 12.5, 15, 17.5, and 20 % w/v. Polymer solution was then subjected to the electrospinning process to evaluate the morphology of the electrospun produced via optical microscope. Simultaneously, the formation of electrospinning jet is observed with portable digital microscope. The morphology of the electrospun fibres, especially the fibre and bead diameter are analyzed using image analysis software, ImageJ. From this research, it is found that at voltage of 10 and 12.8 kV, a stable electrospinning jet can be formed which consists of 'Taylor cone', straight jet, and plume. Concentration from 7.5–20 % w/v were able to form electrospun fibres, yet only 12.5 and 15 % w/v PLA concentrations can produce an effective electrospun fibres with beads diameter of 3393 nm and 3642 nm, respectively. Also, the number of beads for both concentrations are 34 and 19, respectively. Since the main criteria in producing electrospun fibres is no beads or small and minimal beads at best, therefore 12.5 and 15 % w/v PLA concentration are considered as efficient electrospun fibres.

Keywords: Electrospinning; Polylactic acid; Dimethylformamide; Jet formation; Fibre diameter; Bead diameter

1.0 Introduction

A nonwoven web is a sheet or mat of fibres connected together by physical entanglements or adhesion between individual fibres without any knitting or stitching. There are several methods or techniques that can be used to produce porous fibre for instance electrospinning, wet spinning, and moulding. However, electrospinning is an efficient method as it is a versatile, low-cost, and effortless method in producing nanoporous membranes [1, 2]. Electrospinning uses electric force to draw charged threads of polymer solutions towards a collector, such as rotating drum or metal plate, where strands of fibres are formed. Fibre produced is also known as electrospun fibre. The ability to produce a porous fibre with high surface area and small pore diameter from hundreds nanometre to several micrometre render electrospinning method more attractive to meet further application demands in various fields [1].

Key factors in producing ideal electrospun porous fibres are types of solvent, type of polymer, concentration of both polymer and solvents, as well as amount of voltage supplied [3]. Voltage and flow rate used are crucial in electrospinning process to produce a stable jet which led to the formation of fibre. The voltage supplied is connected to the tip of the syringe needle and the metal collector to electrify the polymer solution in forming a stable spinning jet towards the metal collector. Threshold voltage needs to be reached to supply electrical charges to the polymer solution at the needle tip. This is supported by Nayak [4] which claimed that inability of forming a spinning jet is due to the low voltage The metal collector is placed at an optimum distance. The ejected spinning jet or known as 'Taylor cone' formed due to attached to the surface tension and viscoelastic stresses [5, 6]. Electrospinning jet is divided into three parts which are Taylor cone, jet, and plume. Taylor cone occurs at the tip of the needle where it resembles a cone then tapered into a straight jet and ends with fan-shaped aerosol called plume. Plume occurs when the electrostatic became large enough to cause the jet to extrude from the Taylor cone which induce the jet to split that simulates bending and whipping [7].

Synthetic polymer has higher stability compared to natural polymers [8]. Thus, this study will be focused on polylactic acid (PLA), a synthetic polymer, as it possess positive characteristics such as low toxicity, renewable, as well as excellent biodegradability and biocompatibility polymer [3, 9]. Selection of solvent is important to dissolve PLA as well as to form a stable electrospinning jet. NatureWorks, one of the main producers of polymer which derived from plant resources has listed several solvents which are considered as a good solvent to dissolve PLA. The list includes dichloroethane, dimethylformamide (DMF), toluene, and heptanol. Several researchers also claimed that DMF is the best choice to pair with PLA along with acetone, ethanol, and chloroform [3, 9-11].

DMF is widely used in the process of electrospinning involving PLA due to its' ability to dissolve PLA, however the electrospun produced contains defect which is bead. Casasola et al [10] found that beaded fibre can be observed at all concentration when electrospun with PLA. Yet, to this date, there is limited study that discuss the effect of concentration on the bead formation, specifically beads diameter. Most researchers focused on how to inhibit the formation of beads when using DMF as a solvent. For example, Jahangir et al [11] found out that, beads-free electrospun fibre can be produced when AC is paired with DMF as a solvent. We hypothesized that the increase in concentration of PLA will increase the diameter of the beads as well as the fibre diameter. In this research, six polymer solution made up of PLA/DMF with different concentration ranging from 7.5–20 % w/v were prepared to investigate the effect of concentration on the diameter of beads. The polymer solutions were then subjected to the electrospinning process to produce electrospun fibres. Simultaneously, the formation of electrospinning jet with different concentration of PLA at fixed flow rate and voltage was observed. Then, the morphology of the electrospun fibres was evaluated and analysed.

2.0 Materials and methods

2.1 Materials

Polylactic acid (PLA) pellets was supplied by NatureWorks, USA. PLA used was 4043D which is for general film purposes. Solvents used was N, N-Dimethylformamide (DMF), molecular weight (M_W) of 73.09, which is an analytical grade from R&M Chemicals, Malaysia and were used without further purification.

2.2 Sample Preparation

The PLA/DMF solutions were prepared for PLA concentration of 7.5, 10, 12.5, 15, 17.5 and 20 % w/v. For 7.5 % w/v, 1.5 g of PLA pellets was dissolved in 20 ml of pure DMF. An incubation shaker (KS 3000 I Control, IKA, Germany) was used to dissolve PLA. The temperature was set at 60 °C with a rotating speed of 150 rpm. The duration of the dissolution was 24 hours which is to obtain a completely homogenous solution.

2.3 Electrospinning Process

The PLA/DMF solution prepared was then subjected to the electrospinning process. 4 ml of PLA/DMF each of the concentration was placed in a 5 cc BD-plastic syringe with an 18G blunt needle tip (Outer Diameter: 1.27 mm and Inner Diameter: 0.84 mm). Next, the syringe was placed in a syringe pump (SP20, Nanolab Instrument, Malaysia). An applied voltage of 10 and 12.8 kV (depends on concentration) was supplied from a high voltage power supply (PS35-PV, Nanolab Instrument, Malaysia) with a flow rate of 1.0 ml/hr. Copper plate covered with aluminium foil which served as a collector was placed 10 cm from the tip of needle. Crocodile wire was used to supply voltage to the tip of the needle and collector. The experiment was carried out in an acrylic chamber at a room condition (28 °C, 66 % RH) to maintain the temperature and humidity. The digital camera microscope (X4, Shenzhen Haiweixun Electronics Co. Ltd., China) was placed near the needle to observed the formation of the electrospinning. The duration of electrospinning process was fixed at 4 hours to obtain a thicker and refined electrospun fibres.

2.4 Electrospun Fibres Evaluation and Analysis
The collected electrospun fibres was placed in a desiccator for 24 hours to remove excess solvent from the fibres. Then, the electrospun fibres was extracted from the aluminium foil by using forceps and placed onto a glass slides for observation under Optical Microscope (Axio Lab. A1, Carl Zeiss Microscopy LLC, USA). The images taken from the Optical Microscope were analysed using ImageJ (version 1.8.0_172, University of Wisconsin, USA) to study the presence of beaded fibres and the diameter of the fibres. Also, Martin's diameter (d_M) procedure was used to measure the diameter of the beads by using the ImageJ.

3.0 Results and Discussion

3.1 Formation of electrospinning jet
Figure 1 shows the formation of electrospinning jet of 12.5 % w/v PLA concentration in PLA/DMF polymer solution. Figure 1 a) depicts the formation of Taylor cone which tapered into a straight jet. Although the straight jet is facing upward, but the jet is stable and does not waver which can form plume or spinning polymer as shown in Figure 1 b). The formation of electrospinning jet for all concentration were the same, however the voltage supply varied for some concentration. For polymer concentration ranging from 12.5–20 % w/v, the electrospinning jet can be formed with voltage of 12.8 kV and flow rate of 1.0 ml/hr. As for the 7.5 and 10 % w/v, the voltage supplied is 10 kV. The range of voltage used in the past studies is between 8.5–20 kV [3, 12], therefore all the concentrations fall into the range. Voltage supplied is needed to break the surface tension which leads to the formation of electrospinning jet while evaporation rate of the solution is important factor in the determining the behavior of the electrospinning jet [13]. Therefore, the different in voltage used is to prevent the evaporation from taking place at the needle tip. From the experiment, it was observed that the higher the concentration, the higher the evaporation rate of the polymer solution. When the evaporation occurs at the tip of the needle, the polymer solution will harden and has the potential to clog the needle tip. Also, Zhargam et al [14] claimed that the stabilities of the electrospinning jet, particularly the Taylor cone affect the uniformity of the electrospun fibres.

IOP Conf. Series: Materials Science and Engineering **778** (2020) 012087 doi:10.1088/1757-899X/778/1/012087

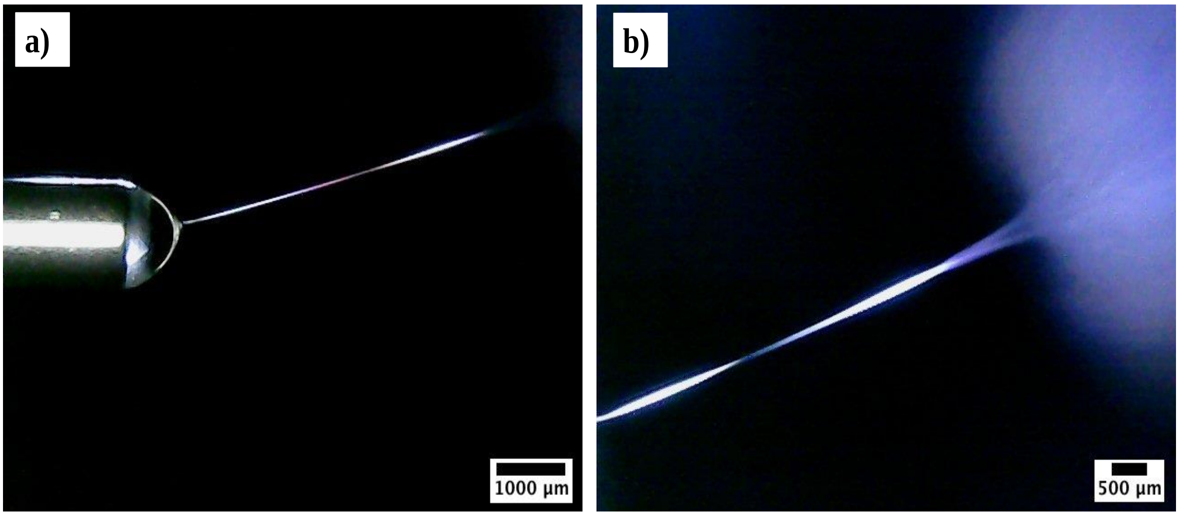

Figure 1: Electrospinning jet of 12.5 % w/v PLA concentration in PLA/DMF solution, a) Taylor cone at the tip of the needle and b) electrospinning plume.

3.2 Effect of Concentration on Fibre and Bead of Electrospun fibres

The morphology of the electrospun fibres for 12.5 and 15 % w/v of PLA are shown in Figure 2 a) and b), respectively. Based on the images, it can be noted that the electrospinning of PLA/DMF produced continuous fibres. Nonetheless, all concentrations studied produced continuous fibres when observed using the Optical Microscope. However, for 12.5 and 15 % w/v PLA concentration, the fibre produced contained less beaded fibres when observed using the Optical Microscope. Small beads can be seen scattered at almost all fibres at PLA concentration of 7.5 and 10 % w/v while beads formation can hardly be seen on electrospun fibres at PLA concentration of 17.5 and 20 % w/v. However, the size of the beads was a lot bigger compared to the rest. As for the orientation of the fibres, Figure 2 show 15 % w/v PLA concentration showed a slightly aligned fibres compared to 12.5 % w/v PLA concentration, where the orientation of the fibres is more random. Also, based on the observation using Optical Microscope, it can be noted that PLA concentration of 15 % w/v and above produced slightly aligned fibres while PLA concentration of 12.5 % w/v and below produced more random fibres. Despite concentration has a slight effect on the orientation of fibres, the main factor of producing aligned fibres is the type of collector [1].

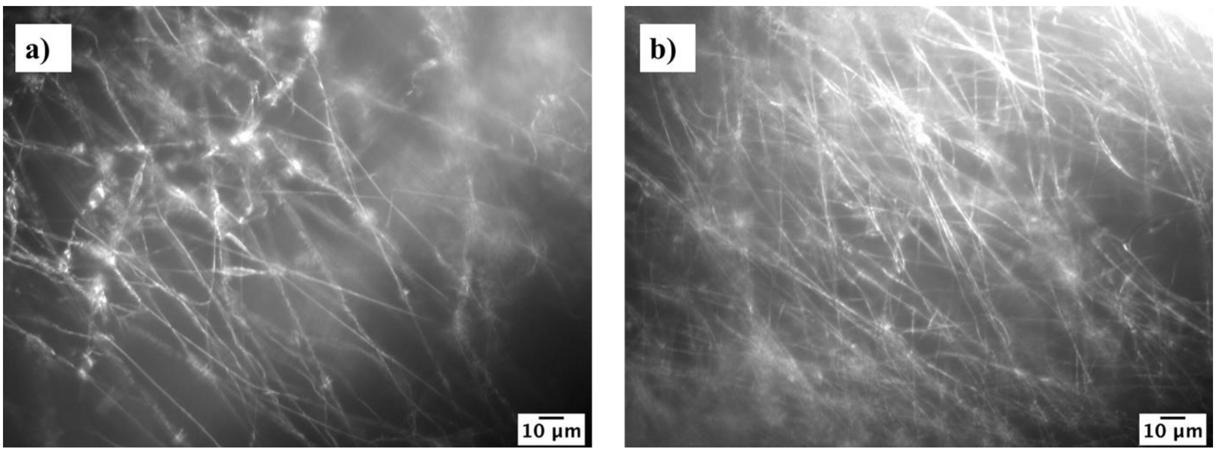

Figure 2: Electrospun fibres of PLA/DMF a) PLA concentration of 12.5 % w/v and b) PLA concentration of 15 % w/v.

The fibres diameter as well as beads diameter were analyzed by using ImageJ. Table 1 shows the fibres diameter (d_f), beads diameter (d_M), as well as the number of beads on the electrospun fibres for all PLA concentration. The electrospinning of PLA/DMF can yield fibre diameter in the nano-scale,

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which is from 249–357 nm. Both fibres and beads diameter increase with concentration. However, beads diameter shows major increments compared to fibre diameter. Zhu et al [15] stated that, the diameter of the fibres increased greatly with concentration although the range of standard deviation was big. Although the higher concentration led to bigger beads diameter, yet the number of beads decreased vastly.

Martin's diameter is used to measure the diameter of the beads because the shape of the beads is more towards ellipse. d_M is the length of the line parallel to a given reference line that divides the area of the particles into two equal parts [16]. Presence of beads is considered as a defect towards electrospun fibres and can decrease its' efficiency in regard to several application including air filtration and drug delivery, however, best case scenario next to it is to choose an electrospun fibre with small and minimal beads. Based on Table 1, the highest average beads diameter is from PLA concentration of 20 % w/v (8235 nm), followed 17.5 % w/v (5600 nm), 15 % w/v (3642 nm), 12.5 % w/v (3393 nm), 10 % w/v (2989 nm), and 7.5 % w/v (2534 nm). Figure 3 represents the box and whisker plot for the beads' diameter for all concentration. Based on Figure 3, PLA concentration of 20 % w/v shows the largest variation of values from the median and 7.5 % w/v shows the smallest variation of values from the mean. Although the number of beads for 20 and 17.5 % w/v PLA concentration are the smallest, yet the diameter of the beads is the highest with large standard deviations which are ± 2809 nm and ± 1179 nm, respectively. However, since the number of beads present on 7.5 % and 10 % are the highest (460 and 302, respectively) and the diameter of beads for 20 and 17.5 % w/v are the largest (8235 and 5600 nm), therefore these concentrations are not suitable to produce electrospun fibres. As for 12.5 and 15 % w/v PLA concentration, the average diameter of beads are 3393 nm and 3642 nm with standard deviation of 972 nm and 699 nm, respectively. Also, the number of beads presence for both of the concentration is > 90 % smaller compared to 7.5 and 10 % w/v PLA concentration. Since there is no thorough discussion about the beads' diameter on the electrospun of PLA/DMF in Casasola et al [10], therefore 12.5 and 15 % w/v PLA concentration are considered efficient in producing an electrospun fibres. The concentrations are considered efficient based on the number of beads present as well as the diameter of the bead.

Table 1: Average fibres diameter, averages bead diameter, and number of beads for PLA concentration ranging from 7.5–20 % w/v.

Concentration, (%)	Average fibres diameter, d_f (nm)	Average Martin's diameter of beads, d_M (nm)	Number of beads
7.5	249 ± 25	2534 ± 188	460
10.0	266 ± 35	2989 ± 648	302
12.5	291 ± 33	3393 ± 972	34
15.0	294 ± 20	3642 ± 699	19
17.5	316 ± 22	5600 ± 1711	11
20.0	357 ± 30	8235 ± 2809	8

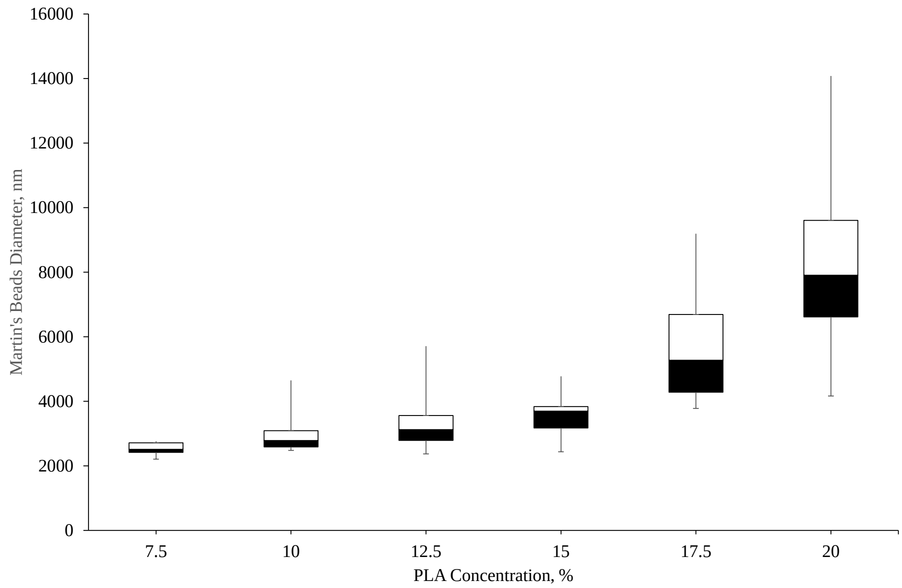

Figure 3: Box and whisker plot of beads diameter for 7.5–20 % w/v PLA concentrations.

4.0 Conclusions

The formation of stable electrospinning jet requires an optimum amount of voltage supplied to break the tension of polymer solution at the needle tip. Taylor cone was successfully formed for all concentration (7.5, 10, 12.5, 15, 17.5, and 20 % w/v) when it reached optimum voltage which then tapered into a straight jet. The bending and splitting of straight jet will formed a fan-like aerosol which is called a plume.Fibre diameter as well as bead diameter are greatly influenced by the concentration of polymer (PLA), especially bead diameter. As concentration increases, the diameter of fibre and bead also increases. Although concentration of PLA ranging from 7.5–20 % w/v in DMF solvent produced beaded fibres which can hinder the capability of the electrospun fibres, however 12.5 and 15 % w/v PLA concentration have been identified as the more efficient PLA concentration in producing electrospun fibres in terms of the number of beads present as well as the diameter of the beads. An improvised electrospinning polymer solution needs to be further studied to produce a bead-free electrospun fibres.

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Acknowledgement
This work was supported by Japan International Cooperation Agency (JICA) Grant. Authors gratefully acknowledge Air Resources iKohza members as well as Engineering Materials and Structures iKohza members for their help and support.