A study of free surface electrospinning process to enhance and optimize the nanofibre production

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***Abstract* -- Electrospinning is a simple and inexpensive process that produces continuous nanofibres from the submicron diameter scale down to the nanometer diameter scale through an electrically charged jet of polymer solution. Previously, most of the electrospinning experiments have been carried out using single-needle arrangements. However, the low fluid throughput in needle spinning has limited the industrial use of needle schemes. In this research, a centrifugal electrospinning scheme was developed to produce non-woven webs of continuous nanofibres from polymer solutions. The system was optimized to enhance the production rate with controlled morphology and size of nanofibres.**

***Index Terms*--Rotary atomization, Electrospinning, throughput, nanofibres, ligament formation, free surface electrospinning**
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I. INTRODUCTION

Electrospinning is a simple and inexpensive process that produces continuous nanofibres from the submicron diameter scale down to the nanometer diameter scale through an electrically charged jet of polymer solution. To date, a significant progress has been made, including the understanding of the spinning mechanism, fabrication of various nanofibre assemblies, and coaxial electrospinning [1]. Previously, most of the electrospinning experiments have been carried out using single-needle arrangements. However, the low fluid throughput in single-needle spinning has limited the industrial use of single-needle schemes. To meet high liquid throughput requirements, several multi-jet schemes have been tested recently [2-5]. These schemes are technologically inconvenient due to possible clogging. In addition, it is generally accepted that eletrospinning using needles, which is defined as capillary spinning, leads to low productivity of nanofibres. Alternatively, in principle, it is possible to obtain self-organized, multiple electrically driven jettings from planar and cylindrical surfaces by applying very high electric fields. Recent experimental and theoretical studies have demonstrated the high fibre production rate to an industrial scale by free surface electrospinning using viscoelastic polymeric liquids. For example, a needleless approach for nanofibre mass production using the combined effects of magnetic and electric fields acting on a magnetic fluid and polymer solution layers has been reported [3]. Jirsak et al. demonstrated a device known as Nanospider^{TM} based on a rotating cylinder-solution feeding system capable of producing nanofibres at a reasonable rate [6]. More recently, Lin et al. designed a disc electrospinning setup, where a rotating disc was used to replace the cylinder in Nanospider^{TM} [7]. In addition, Thoppey et. al have demonstrated a novel needle free electrospinning configuration using an edge-plate geometry. The report has been mentioned that this configuration can directly be used to fabricate high quality nanofibres from unconfined fluids without the possibility of clogging. Moreover, it has been claimed that the fabrication rate of the edge spinning apparatus is 5 times higher than to a typical needle based electrospinning apparatus [8].

Rotary atomizers have been used for at least 25 years for the applications of fine droplet formation such as pesticide spraying systems. However, more recently, the same concept has been used by several researchers for electrospinning applications [9-12]. The process combines the concepts of both centrifugal spinning and electrospinning that results in very high fibre throughput. In addition, rotary spinning has many other advantages compared to other nanofibre fabrication methods: (a) the technique does not necessarily require high-voltage electric fields, (b) straightforward implementation, (c) applicability for both solution and melt spinning, and (d) facility to fabricate nanofibres into any arbitrary shape with modified collectors.

In this research, a novel centrifugal electrospinning scheme, which is capable of producing non-woven webs of continuous nanofibres with controlled morphology and size from polymer solutions with the application of high electric field, was developed to enhance the production rate of nanofibres. This novel scheme is capable of producing nanofibres at a reasonable rate compared to the conventional capillary schemes. The scheme was investigated by varying the processing conditions and different polymer solutions to obtain the optimum operating regime with high quality nanofibres.

II. Rotary Atomization

Hinze et. al have observed three different modes of spray formation that may take place around the edge of a spinning disc [13]. The transition from one mode to another was governed by the flow rate of a given liquid and rotational speed of the disk. Fig. 1 shows the first mode of operation where drops of fairly uniform size are thrown directly from the edge of the rotating disc. Hinze et. al have named this mode as direct drop formation mode (Mode 1) [13, 14].

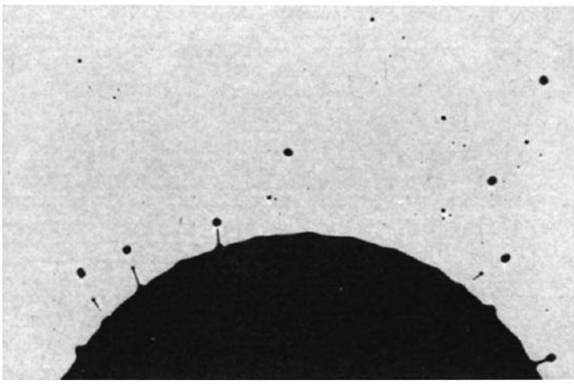

Fig. 1. Direct drop formation mode [14].

If the liquid flow rate on to the disk or the rotating speed of the disk is increased, the direct drop formation mode of the disk is transformed into ligament formation mode (Mode 2) as shown in Fig. 2. Ligament formation mode generates smaller droplets with a narrow distribution of the droplet size.

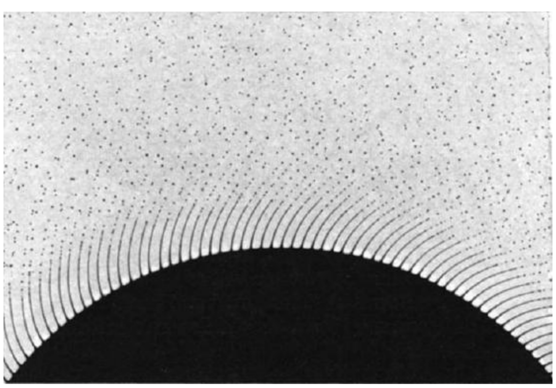

Fig. 2. Ligament formation mode [14].

If the liquid flow rate or the rotation speed of the disc is further increased, the ligaments are transformed into a thin film of fluid as shown in Fig. 3 (Mode 3). This mode of operation creates a significant amount of non uniformity of the droplet formation. Therefore, this mode of operation is not desirable to produce fine droplets with sufficient uniformity.

If a viscoelastic polymer solution is used for rotory atomization, then it generates continuous fibres instead of droplets. However, all three modes of operation would still be applicable.

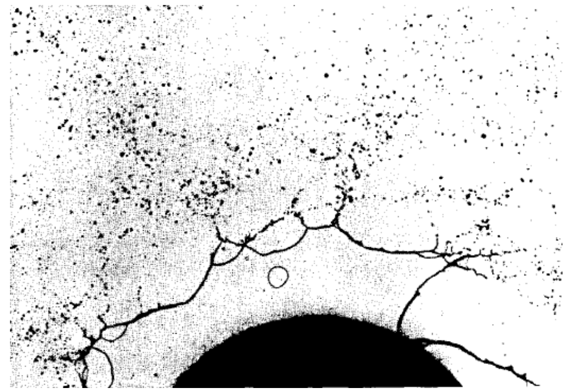

Fig. 3. Sheet (film) formation mode [14].

III. Experimental Section

A. Material preparation

Polyethylene oxide (PEO) with an average molecular weight of 600,000 purchased from Aldrich® was chosen to prepare the polymer solutions. PEO fibres were electrospun using 2.5%, 5%, and 7.5% (w/w) concentrations of PEO in de-ionized water. In addition, PEO/ethanol/water solutions were investigated using the novel electrospinning scheme. PEO was dissolved in aqueous ethanol with a weight ratio of ethanol/water of 60:40. Thereafter, PEO fibres were electrospun using a 5% (w/w) concentration of PEO in prepared aqueous ethanol solution. The solutions were stored at room temperature and all electrospinning experiments were carried out at room temperature and atmospheric air.

B. Experimental Setup

Fig. 4 illustrates the experimental setup that was used to perform the electrospinning experiments. The electrospinning apparatus will not be disclosed in detail due to the proprietary nature of the research. Spellman high voltage DC power supply was used to apply the high voltage between the needle and the collector plate. Thereafter, the ligament and film

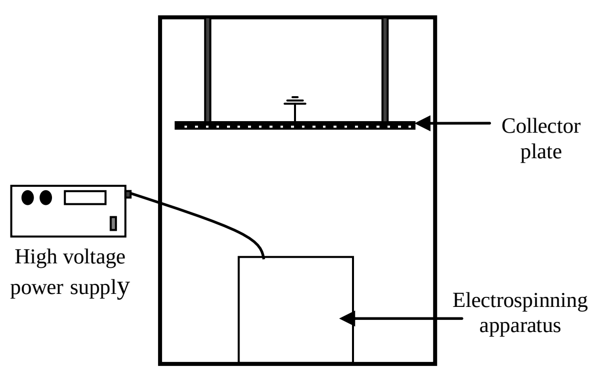

Fig. 4. Schematic drawing of the experimental setup.

formation modes of the electrospinning setup was investigated by maintaining the applied voltage at a constant value of 25kV. The flow rate of the polymer solution was varied from 0.5ml/min to 5ml/min. The rotating speed of the electrospinning apparatus was varied from 500rpm to 3000rpm. The distance between two electrodes was kept at a constant value of 150mm.

IV. Results and Discussion

During centrifugal electrospinning experiments, a region of wet fibres is observed inboard of the collector plate outer diameter when the spinning apparatus rotor is charged with a positive high voltage with a grounded collector. The larger ligaments move away from the spinning rotor due to the centrifugal force and these ligaments produce the wet fibre regions as a result of inadequate evaporation of the solvent. This behavior is dominant when the system operates at the sheet formation mode. This is a major drawback of the centrifugal electrospinning apparatus.

Table 1 shows the variation of the characteristics of the collected fiber mat with the variation of the flow rate of the polymer solution from 0.5ml/min to 5ml/min. As shown in the table, dry nanofibres were collected in the flow rates of 0.5ml/min, 1.0ml/min, and 2.0ml/min. Therefore, it indicates that the system is transforming from Mode 1 to Mode 2. However, when the flow rate of the polymer solution is above 2ml/min, both dry and wet fibres are collected on the collector. This behavior was dominant at higher flow rates (ex. 5ml/min). This concludes the transformation of the system from Mode 2 to Mode 3 at higher flow rates.

TABLE I
VARIATION OF THE CHARACTERISTICS OF THE COLLECTED FIBRES WITH THE VARIATION OF SOLUTION FLOW RATE USING A 5 (WT%) PEO SOLUTION

Flow rate of the polymer solution (ml/min)	Rotating speed of the disk (rpm)	Characteristic of collected fibres
0.5	1500	Dry fibres
1.0	1500	Dry fibres
2.0	1500	Dry fibres
3.0	1500	Mostly dry fibres
4.0	1500	Dry and wet fibres
5.0	1500	Dry and wet fibres

Table II shows the collected nanofibre characteristics by varying the rotating speed of the centrifugal electrospinning setup. As shown in the table at very low speeds (500rpm), the collected fibers have a wet region due to the formation of larger ligaments. Larger ligament slows the solvent evaporation process resulting wet fibre collection. However, the fibre characteristics change from wet to dry with the increase of the rotational speed as a result of formation of finer ligaments during the process. When the rotational speed is increased further, the characteristics of fiber formation is changed again form dry to wet due to the transformation of the system from Mode 2 to Mode 3.

TABLE II
VARIATION OF THE CHARACTERISTICS OF THE COLLECTED FIBRES WITH THE VARIATION OF ROTATION SPEED OF THE ELECTROSPINNING APPARATUS USING A 5 (WT%) PEO SOLUTION

Rotating speed of the disk (rpm)	Flow rate of the polymer solution (ml/min)	Characteristic of collected fibres
500	2.0	Dry and wet fibres
1000	2.0	Dry fibres
1500	2.0	Dry fibres
2000	2.0	Dry fibres
2500	2.0	Dry and wet fibres
3000	2.0	Dry and wet fibres

Table III shows the effects of type of solution on the collected nanofibre characteristics. The less viscous 2.5(wt%) PEO solution was formed dry and wet fibres due to the increased flow rate during electrospinning. It indicates that the system was operating in Mode 3 in these conditions. When the solution is changed to 5 (wt%) PEO solution, the resultant fibres are mostly dry due to the decreased flow rate with increasing viscosity. This shows the transformation of the mode of operation from Mode 3 to Mode 2. If the viscosity of the polymer solution is increased further using a 7.5 (wt%) PEO solution, the fiber formation stops due to the increased viscosity of the polymer solution. PEO polymer solution that was formulated using aqueous ethanol produced completely dry fibres due to the increased volatility during the electrospinning process. Fig. 5 shows an SEM image of nanofibres that was collected during dry fibre formation. The fibre diameters (~300nm) are comparable to the diameters of fibres that were formed during needle electrospinning.

TABLE III
CHARACTERISTICS OF THE COLLECTED FIBRES WITH THE VARIATION OF POLYMER SOLUTION

Polymer solution	Rotating speed of the disk (rpm)	Flow rate of the polymer solution (ml/min)	Characteristic of collected fibres
2.5% PEO	1500	3.0	Dry and wet fibres
5.0% PEO	1500	3.0	Mostly dry fibres
7.5% PEO	1500	3.0	Difficult to spin
5.0% PEO in aqueous ethanol	1500	3.0	Dry fibres

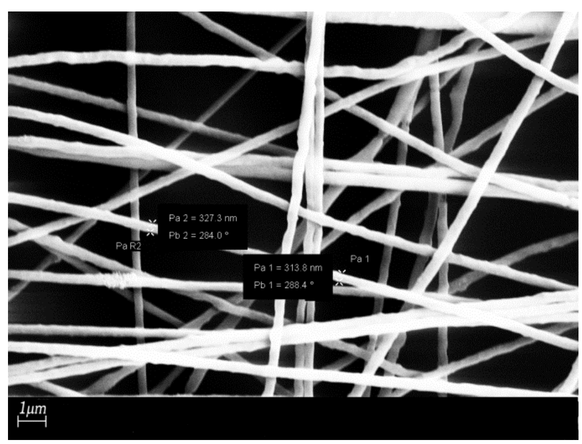

Fig. 5. SEM image of centrifugally electrospun PEO nanofibres.

V. CONCLUSIONS

A centrifugal electrospinning apparatus was designed to increase the throughput of the electrospinning process. The apparatus was able to produce nanofibre morphologies similar to the needle electrospinning systems with higher flow rates. A parametric investigation was carried out to determine the operating regime of the apparatus with building analogy to the rotary atomization.

REFERENCES

[1] S. Ramakrishna, K. Fujihara, W.E. Teo, T.C. Lim, and Z. Ma, *An Introduction to electrospinning and nanofibers*. Singapore: World Scientific Publishing Co. Pte. Ltd., 2005.

[2] Y. Yang, Z. Jia, Q. Li, L. Hou, H. Gao, L. Wang, and Z. Guan, "Multiple jets in electrospinning," in Proc. *2006 8th International conference on properties and applications of dielectric materials*, pp. 940-943.

[3] A. L. Yarin and E. Zussman, "Upward needleless electrospinning of multiple nanofibers," *Polymer*, vol. 45, issue 9, pp. 2977-2980, Mar. 2004.

[4] S.A. Theron, A.L. Yarin, E. Zussman, and E. Kroll, "Multiple jets in electrospinning: experiment and modeling," *Polymer*, vol. 46, issue 9, pp. 2889–2899, Apr. 2005.

[5] O.O. Dosunmu, G.G. Chase, W. Kataphinan, and D.H. Reneker, "Electrospinning of polymer nanofibres from multiple jets on a porous tubular surface," *Nanotechnology*, vol. 17, pp. 1123–1127, Feb. 2006.

[6] O. Jirsak, F. Sanetrnik, D. Lukas, Z. Na, and V. Koteck, CZ Patent WO2005024101 2005.

[7] F.L. Zhou, R.H. Gong, and I. Porat, "Mass production of nanofibre assemblies by electrostatic spinning," *Polym Int*. vol. 58, pp. 331–342, 2009.

[8] N. M. Thoppey, J. R. Bochinski, L. I. Clarke, and R. E. Gorga, " Unconfined fluid electrospun into high quality nanofibers from a plate edge," *Polymer*, vol. 51, pp. 4928-4936, July 2010.

[9] M. R. Badrossamay, H. A. McIlwee, J. A. Goss, and K. K. Parker, " Nanofiber Assembly by Rotary Jet-Spinning," *NanoLetters*,vol. 10, no. 6, pp. 2257-2261, May 2010.

[10] C. C. Liao, C. C. Wang, C. Y. Chen, and W. J. Lai, "Stretching-induced orientation of polyacrylonitrile nanofibers by an electrically rotating viscoelastic jet for improving the mechanical properties," *Polymer*, vol. 52, pp. 2263-2275, Mar. 2011.

[11] "Centrifugal spinning of virgin and recycled thermoplastic polymer waste", Tech. Rep., http://www.leeds.ac.uk/textiles/CTT/CENTRIFUGAL%20SPINNING%20OF%20%20THERMOPLASTIC%20POLYMERS%20.pdf

[12] J. Engström and B. Hagström, " Centrifugal spinning of nanofiber webs - A parameter study of a novel spinning process," *Textile Jornal*, pp. 82-91, 2009.

[13] J. O. Hinze, and H. Milbom, "Atomization of liquids by means of rotating cups". *J. appl. Mech.*, vol. 17, pp. 145-153, 1950.

[14] A. R. Frost, "Rotary Atomization in the Ligament Formation Mode," *J. Agri. Engng. Res.*, vol. 26, pp. 63-78, 1981.