

A study on the industrialization of PEO nano-fiber film by electro-spun process

Chih-Hsiang Lin^a, Chin Pan Huang^a, I-Shou Tsai^a, Tien-Wei Shyr^a, Wei-Cheng Chu^b

^a Graduate Institute of Textile, Feng-Chia University, No. 100 Wenhwa Rd., Seatwen, Taichung, Taiwan (R.O.C.)

^b Department of Fashion Design, Shu-Te University, No. 59, Heng-Shan Rd., Yanchao, Kaohsiung, Taiwan (R.O.C.)

Abstract

Electro-spun technical principles had been studied and applied at present. But there were some problem need to be surmounted for industrialization, for example, low throughput, variation of fiber diameter and basis weight.

This study included three steps for industrialization of electro-spun process to solve above problems for nano-fiber film. The condition of 5% wt of PEO solution (PEO is 300,000 g/mol) was used in this study. Firstly, the suitable collector and supporting media were established through full-factorial experiments and images analysis. A non-embossed spun-bond nonwoven was used as a supporting media and a flat metal plate was selected as a collector in this study. Secondly, the optimum electro-spun parameters were found by using a full-factorial experiment for varied with working voltage, throughout, CSD by SEM analysis.

The results was shown that the average of fiber diameter was 578.69 nm and its CV% of fiber diameter was 13.46% in the process parameters of 42 cm CSD for 41 kV working voltage and 0.3573 mL/min throughput. Third, trial-run with the result of first and second steps, the filtration efficiency was 91.2% with pressure drop 13.8 mm-H₂O by TSI 8130 (32 LPM, 5 % NaCl) analysis.

Keywords: Electro-spun; Industrialization; Distribution evenness; Nano-fiber film; Image analysis; Point discharge

1. Introduction

Electrospinning is a unique process in that it is able to produce polymer fibers with diameters ranging over several orders of magnitude, from the micrometer range typical of conventional fibers, down to the nanometer range. Owing to the smallness of their diameters, electrospun fibers possess unusually large surface-to-volume ratios and are expected to display morphologies and material properties very different from the conventional fiber. Additionally, electrospun fibers in the form of nonwoven fabrics offer unique capabilities to control pore size. Electrospinning is a fast and simple process. Since it only requires small quantities of polymer, it can rightfully be termed as a microprocessing technique.

Depending on the solution properties, the throughput of single-jet electrospinning system ranges from 10 μ L/min up to 10 mL/min. This low fluid throughput may limit the industrial use of electrospinning.

In general, electrospinning can manufacture fibres which are not only very thin, but also have a smooth lateral surface and a uniform profile. Unfortunately the efficiency of this method is not high. In most published works devoted to investigating electrospinning, the authors have used experimental stages equipped with only a single spinning point. Only Ding et al. [1] used a few syringes simultaneously for electrospinning from different polymer solutions, and Schiffman et al. [2] applied a system of a 24-gauge needle to electrospin PLA solution into mats.

Multiple nozzles have also been introduced in electrospinning as a means to increase production rate [3–7]. In addition to the increase in production rate, multiple nozzles have been used in electrospinning to make multi-component blend nanofibrous mats [5,8,9].

The aim of the present work is the investigation of electrospinning of polymer nanofibers from spinneret (112 holes / 7cm) and the experimental about the effect of vary electrospinning parameters for electrospun fiber distribution evenness.

2. Experiment

2.1 Materials

- (1) PEO (polyethylene oxide): Alkox-E30, Tonen
- (2) IPA (iso-propyl alcohol): PL-06642, Nihon Shiyaku
- (3) pure water
- (4) calendering black spunbond nonwoven: 20 g/m², :Universal Incorporation
- (5) embossed black spunbond nonwoven: 15 g/m², Freudenberg Far Eastern Spunweb Co., Ltd.
- (6) stainless steel plate
- (7) 10 mesh stainless steel net:
- (8) 60 mesh stainless steel net
- (9) stainless steel needle-punch nonwoven: 1200 g/m²

2.2 Apparatus

- (1) Spinneret: ID 0.3 mm, 112 holes/ 7cm (41 holes/inch)
- (2) High voltage power supplier: PS / ER50P06 - YG3A, Glassman high voltage
- (3) Syringe pump: Orin M365, Thermo
- (4) Syringe: 20mL, Top Surgical Taiwan
- (5) Take-up device: 1 cm/min ~ 200 cm/min
- (6) Cross-reciprocating device: 6 rpm, traverse length 5cm

2.3 Analysis Instrument

- (1) SEM(Scanning Electron Microscope) : S3000, Hitachi
- (2) Automated Filter Testers: 8130, TSI
- (3) Electronic Balance: AB204, Mettler-Toledo
- (4) Digital Camera; DSC-P8, 3.2 mega pixels, SONY
- (5) Adobe Photoshop CS 8.0.1

2.4 Electrospinning apparatus setup

Electrospinning setup, see Fig. 1, consists of a high voltage power supplier (1) (PS / ER50P06 - YG3A , Glassman High Voltage), precision syringe pump (2) (ORIN M365, THERMO), positive and negative electrodes, grounded conductive collector(3) , and polymer solution inject into spinneret (4). Some conductive materials will be used as the collector. PEO (Polyethylene oxide) (molecular weight: 300,000 g/mol) was obtained from Tonen in powder form. This material was dissolved in the IPA (iso propyl alcohol) and pure water to form a homogeneous polymer solution required for electrospinning. IPA was the solvents selected for dissolving PEO and were purchased from Nihon Shiyaku.

Homogeneously dissolved polymer solution was taken in the plastic syringe and mounted on the syringe pump. The spinneret, each hole ID 0.3mm, 112 holes/ 7cm (41holes/inch) by our design was used in the experiment. The positive electrode from the high voltage source was connected to the spinneret by means of an alligator clip. The negative terminal of the power source and the collector were grounded. Nanofibres were collected on a smooth supporting screen. Three kinds of materials including stainless steel net, stainless steel plate and stainless steel needle-punch nonwoven were selected as the candidate material for collector. The structure and the morphology of nanofiber web were characterized by using Scanning Electron Microscopy (SEM Hitachi S3000). The images of nanofiber web were computed with digital camera and analyzed by using Photoshop software for fiber distribution.

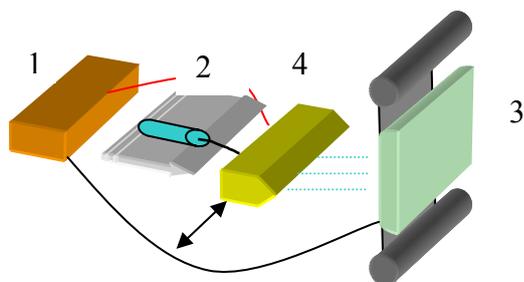


Fig. 1 Schematic drawing of the electrospinning apparatus

2.5 Experiment plan

This study included three stages. Firstly, the suitable collector and supporting media were established through full-factorial experiments and images analysis. Secondly, the optimum electro-spun parameters were found by using a full-factorial experiment for the factors of working voltage, throughput and CSD (distance between spinneret and collector). Third, trial-run parameters were chose according to the result of first and second stages. The trial samples performances including filtration efficiency and pressure drop were tested by TSI automated filter testers.

2.5.1 Stage1 samples preparation

4 types of collectors and 2 types of supporting materials were tried in this stage. Therefore, there are 8 ($2^1 \times 4^1$) kinds assembly.

The electrospinning parameters during stage 1 as follow:

PEO concentration: 5 %

Throughput: 0.3573 mL/min

Working voltage: 40 kV

CSD: 39 cm

BW (basis weight) : about 1.5 g/m²

The sample codes corresponding to the supporting materials and collector were shown as Table 2.1

Table 2.1 The sample codes corresponding to the supporting materials and collector

supporting materials \ collector	embossed black spunbond nonwoven	calendering black spunbond nonwoven
60 mesh stainless steel net	Sample A	Sample B
stainless steel plate	Sample C	Sample D
10 mesh stainless steel net	Sample E	Sample F
stainless steel needle-punch nonwoven	Sample G	Sample H

2.5.2 Stage 2 samples preparation

In order to get the fiber diameter in different parameters assembly, the assembly of collector and supporting material were fixed based on the results in stage 1, and varied the working voltage, throughput and CSD. There are 216 ($6^1 \times 6^1 \times 6^1$) kinds of assembly and are shown as Table 2.2.

The PEO solution concentration is 5 %, each assembly operation time was 10 minutes.

Table 2.2 A list of variable parameters using in stage 2

Working voltage (KV)	throughput (mL/min)	CSD (cm)
35	0.1191	30
37	0.2382	33
39	0.3573	36
41	0.4764	39
43	0.5955	42
45	0.7146	45

To clarify parameters assembly, 3 codes were used to describe sample, for example, code D-3-e represent working voltage is 41kV, throughput 0.3573 mL/min and CSD 42 cm.

Table 2.3 Sample codes for parameters assembly

Working voltage (kV)	Code	Throughput (mL/min)	Code	CSD (cm)	Code
35	A	0.1191	1	30	a
37	B	0.2382	2	33	b
39	C	0.3573	3	36	c
41	D	0.4764	4	39	d
43	E	0.5955	5	42	e
45	F	0.7146	6	45	f

2.5.3 Third stage samples preparation

An optimum trial run parameter was used based on the results of stage 1 and 2 in third stage. The sample performances including the average, standard deviation and coefficient of variance of fiber diameter were tested, and then the take-up speed of supporting material was adjusted for producing of the BW 1.4514g/m², 2.9028 g/m², 4.3542 g/m², 5.8056 g/m² and 7.2572 g/m² of PEO nano-fiber film. Finally, the filtration efficiency and pressure drop were tested by TSI 8130.

3. Result and Discuss

3.1 The effect of various collector and supporting material on fiber deposition distribution

3.1.1 Stage 1 experimental observation

We found the adjacent solution jets from the holes of spinneret were mutually repulsive. This caused the adjacent solution jets direction unpredictable. The uneven deposition blocks were found on the supporting material as shown in Fig. 2.



Fig. 2. Electrospun jet mutually repulsive deposition on supporting material

In a multiple-nozzle arrangement, not only the external applied electric field and self-induced Coulombic interactions, but also mutual Coulombic interactions between different solution jets affect the solution jet path.

The point discharge of static electric in strong electric field is obvious excluding the stainless steel collector (see Fig.3-c), especially for the stainless steel needle-punch nonwoven (see Fig. 3-g, h).

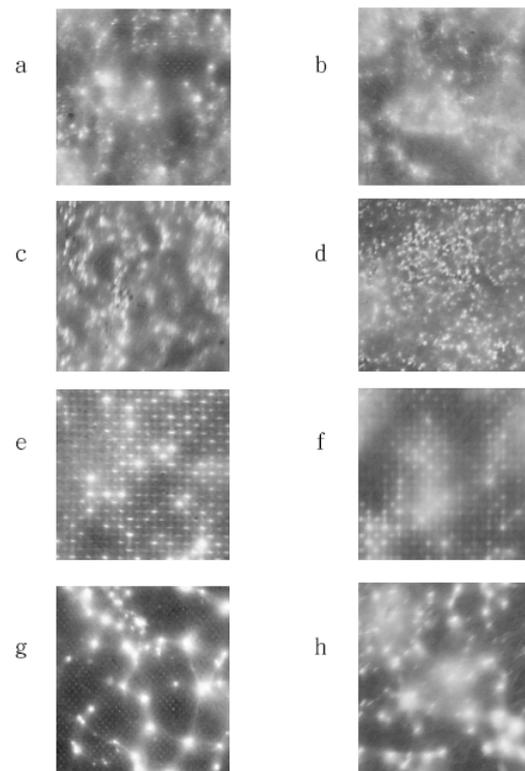


Fig. 3. The distribution of electrospun fiber deposited on different collector and supporting materials

The completeness of the supporting material contacting with collector will affect the electrospun fiber deposition. It was found that a few fiber and even no fiber were deposited on the supporting material in certain of area as Fig. 4 (a), (b). This phenomena result from the protruded bolt on the both side of the collector, therefore, the supporting material can not completely contact with collector.

The point discharge also be found in supporting materials. The supporting materials like nowoven, it has protruded fiber caused the electrospun fiber could not average deposited on nowoven, most of electrospun fiber accumulate to white spots.

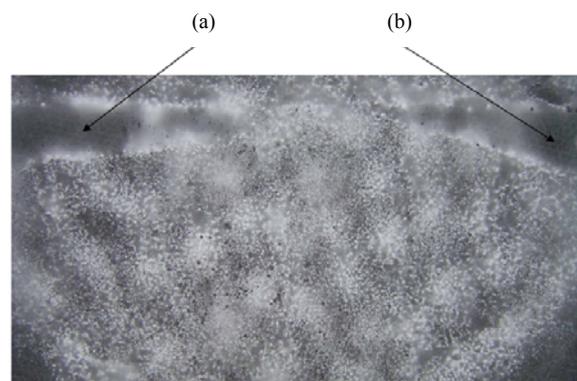


Fig. 4. Electrospun fiber deposited on supporting material

3.1.2 Sample analysis

A sample was cut in size of 25 cm x 50 cm and its image was captured by digital camera. The captured image was transferred into gray level image and further analyzed by Photoshop software.

The gray level image was divided into various size of area, i.e. 2 cm x 2 cm, ...and 10 cm x 10 cm were shown in Fig. 5. They were used to analyze the distribution evenness of fiber deposition in various sampling area for sample A to H.

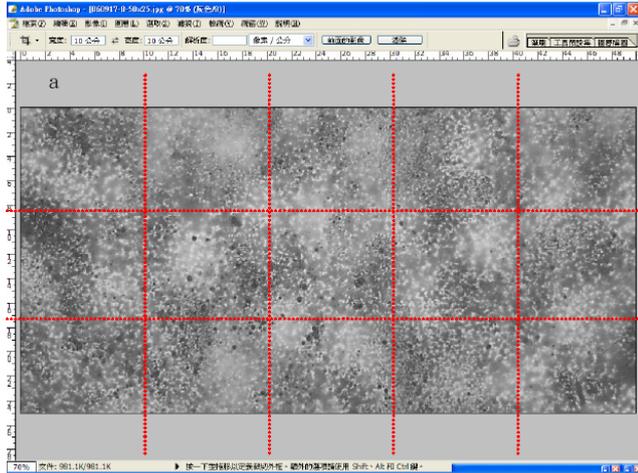


Fig. 5. Sample photo image divided to 15 area

The standard deviation (STDEV) and coefficient of variation (CV %) of average gray level for various sampling area were calculated and shown in Fig. 6 and Fig. 7. The STDEV and CV % of the sample D in various sampling is 1.74 and 2.24 %, respectively, and are smaller than others. Hence, an optimum assembly in stage 1 is sample D, i.e., the calendaring black spunbond nonwoven and the stainless steel plate is the most suitable for next stage 2 and stage 3.

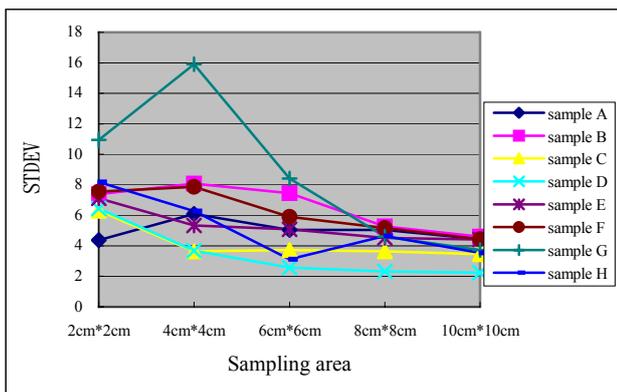


Fig. 6 The standard deviation (STDEV) of average gray level for various sampling area.

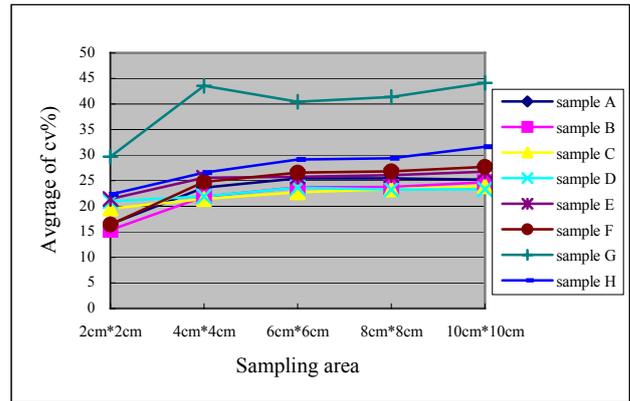


Fig. 7 The CV % of average gray level for various sampling area.

3.2 Stage 2 the effect of change electrospun parameters on distribution and variance of fiber diameter

3.2.1 Experimental observation

In this stage experiment, when the throughput of PEO solution was low, it could not form a continual flow jet. Because the solution solidified too fast, the solidified solution blocked the holes of spinneret. This led to the dripping of solution dropped onto the supporting material.

When the throughput of PEO solution was too high, the molecular cohesive force of PEO solution was higher than the force of static electricity. The PEO solution flow jet will directly, no whipping, deposited onto the supporting material.

In addition, fixed the parameters of throughput and CSD, if rose the working voltage then elongated the whipping distance of solution jet, it means the whipping start point of solution jet will more close to the collector side resulted the solution lack splitting effectiveness. On the contrary, decreasing the working voltage will lead to molecular cohesive force of solution jet was greater than the force of static electricity, this also decreased the solution jet splitting effectiveness.

Rose the CSD, the variance of fiber diameter distribution was decreased. When the parameters of the electric field and throughput keep constant, the solution jet has enough space and released time to split and evaporate, so decrease the variance of fiber diameter.

Synthesize the parameters of the working voltage, throughput and CSD, the D-3-e sample was the optimum assembly, its SEM was shown in Fig. 7. A results was shown that the average fiber diameter was 578 nm and CV% of fiber diameter was 13.46% which with 42 cm CSD, 41 kV working voltage and 0.3573 mL/min throughput. So this assembly of parameters will to run the experiment of stage 3.

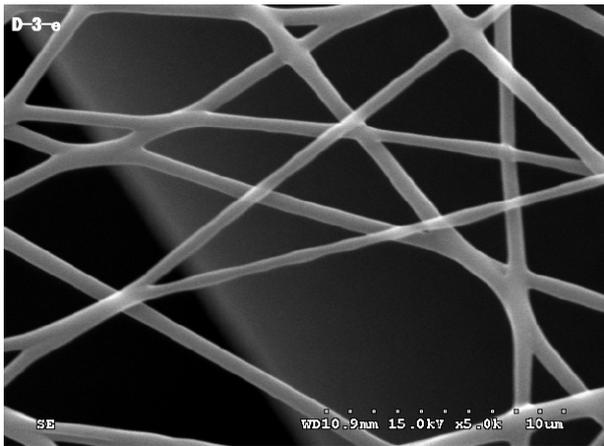


Fig. 7. SEM photograph of Sample D-3-e



Fig. 8 The electrospun fiber could not fully deposit to fill up the aperture at low BW of nanofiber-film.



Fig. 9. The electrospun fiber could fully deposit to fill up the aperture at high BW of nanofiber-film

3.2.2 Samples screening

During the experiment, the holes of spinneret were not outputted solution jet completely. This is due to the vicinity of electric field mutual repulse, especial the neighbor of holes. The phenomena decreased the production of electrospinning. Additionally, the inactive holes generated only gravitationally deformed drops of spinning liquid instead of fibers.

The principle of sample screening as follow:

The total of spinneret is 112 holes, but some experimental parameters assembly could not form the solution jet fully, due to the spinneret holes be blocked. According to the prior experience, the reliability of the solution jet (holes) number of sample was great than 80% of all, i.e. the active holes of spinneret should great than 90 holes. If the solution jet number of sample not achieved the number of mention above then eliminate it.

If the sample, its solution jet has no whipping motion then eliminate it.

If the sample, its solution jet could not to form the continual solution jet then eliminate it.

If the sample, its CSD is too high to collect fiber fully on supporting materials then eliminate it.

The original total of samples number is 256. There was just 48 samples be qualified after sampling screen. The qualified samples were analyzed by SEM.

3.3 Stage 3 — Continual multi solution jet electrospinning

3.3.1 Experimental observation

o the supporting material, i.e. was nonwoven, there were apertures between fiber and fiber, the electrospun fiber could not fully deposit to fill up the apertures at low BW of nanofiber-film, was shown as Fig. 8. When rose BW of nanofiber film, the apertures of nonwoven were filled up gradually, as shown in Fig.9.

3.3.2 Sample analysis

The different BW nano-fiber films were analysed the FE% (percent of filtration efficiency) and ΔP (pressure drop mm-H₂O) by Automated Filter Testers TSI 8130.

TSI 8130 test condition is 5 % NaCl solution, average particle size 0.3 μ m, throughput 32 LPM, pass area 100 cm².

The FE% was proportional to BW of electrofiber film and the higher BW, the FE% increased slowly. When the BW was 7.257g/m², the FE% was 91.2%, the ΔP was 13.86 mm-H₂O, the CV% of FE% was 0.579%.

4. Conclusion

This study was included three stages. Firstly, the suitable collector and supporting material were established through full-factorial experiments and images analysis.

The phenomenon of point discharge of static electricity in strong electric field was very apparent. So the collector and supporting materials as smooth as possible are good to solve the phenomenon. The calendaring black spunbond nonwoven and the stainless steel plate was the most suitable for supporting material and collector. The STDEV within groups was 26.08, the STDEV between groups was 1.74, the CV% within groups was 22.43% and the CV% between groups was 2.24%.

Secondly, the optimum electro-spun parameters were found by using a full-factorial experiment and varied with working voltage,

throughout and CSD. A results was shown that the average fiber diameter was 578 nm and CV% of fiber diameter was 13.46% which with 42 cm CSD, 41 kV working voltage and 0.3573 mL/min throughput.

Third, trial-run parameters used the results of first and second stages, and the FE% and the pressure drop were analyzed by TSI automated filter testers. When the BW was 7.257g/m^2 , the FE% was 91.2%, ΔP was 13.86 mm-H₂O and CV% of FE% was 0.579%.

References

- [1]. Ding B., Kimura E., Sato T., Fujita S., Shiratori S., *Polymer* (2004); 45: 1895-1900
- [2]. Schiffman J.D., and Frey M., Cornell Polymer Outreach Program, Poster Session, May 24, 2004, Available from: <http://www.popsymposium.cornell.edu/careinfo/>.
- [3]. Formhals A. Process and apparatus for preparing artificial threads. US Patent 1934; 1975504. 2898 S.A. Theron et al. / *Polymer* 46 (2005) 2889–2899
- [4]. Simons HL. Process and apparatus for producing patterned nonwoven fabrics. US Patent 1966; 3280229.
- [5]. Smith DJ, Reneker DH, McManus AT, Schreuder-Gibson AL, Mello C, Sennett MS. Electrospun fibers and an apparatus therefore. US Patent 2004; 6753454.
- [6]. Chu B, Hsiao BS, Fang D. Apparatus and methods for electrospinning polymeric fibers and membranes. US Patent. 2004; 6713011.
- [7]. Chung HY, Hall JRB, Gogins MA, Crofoot DG, Weik TM. Polymer, polymer microfiber, polymer nanofiber and applications including filter structures. US Patent 2004; 6743273.
- [8]. Gupta P, Wilkes GL. Some investigations on the fiber formation by utilizing a side-by-side bicomponent electrospinning approach. *Polymer* 2003;44:6353–9.
- [9]. Ding B, Kimura E, Sato T, Fujita S, Shiratori S. Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-solution jet electrospinning. *Polymer* 2004;45:1895–902