Fabrication of Biodegradable PCL Particles as well as PA66 Nanofibers via Air-Sealed Centrifuge Electrospinning (ASCES)

Afsaneh Valipouri and Seyed Abdolkarim Hosseini

***Abstract*—This study presents a method for fabrication of ultrafine polymeric nanofibers as well as nano/micro particles utilizing centrifugal and electrostatic forces simultaneously. To reduce the diameter and variety of nanofibers produced from solid state polymerized PA66, a unique electro-centrifuge spinning device was utilized with a rotating nozzle and collector, while the fabrication process (spinning head) was securely sealed from ambient airflow. An electric field was applied between the nozzle containing the polymer solution and the cylindrical collector. Due to centrifugal force, polymer solution was ejected from the nozzle tip and extended by the centrifugal force as well as the electrical force. The diameters of nanofibers were controlled by adjusting the solution concentration, the rotational speed of the spinning head, the syringe's content and the applied voltage. Field emission scanning electron microscope (FESEM) results demonstrate that this air-sealed centrifuge electrospinning (ASCES) system has a unique ability to produce high quality ultrafine nanofibers from SSP PA66 polymer. The good control of parameters led to the production of fibers with mean diameter of 63 nm. It is also shown that this technique has a good ability to fabricate particles of poly (ε-caprolactone), like electrospray ionization.**

***Keywords*: air-sealed electro-centrifuge spinning, biodegradable particles, solid state polymerized polyamide, ultrafine nanofibers**

I. Introduction

Electrospinning is a suitable technique for producing nanofibers due to its easy manufacturing process, which is governed by several process parameters which can be controlled by the user [1-3]. However, the controlled production of finer polymer nanofibers with a uniform diameter and structure has still remained a challenge [4]. A common method to obtain finer nanofibers is to reduce the concentration of the electrospinning polymer solution as much as possible. However, it needs to exceed a critical concentration to achieve high enough chain entanglements for producing uniform nanofibers [5,6]. Also, it has been found that by increasing the electrical conductivity of the polymer solution, there is a significant decrease in the electrospun nanofiber diameter; since in a solution with low conductivity, there is an insufficient elongation in the jet produced by the electrical force, and bead formation may also be observed [7]. Using additives such as salts [7], polyelectrolytes [8], and ionic surfactants [9] may change the properties of a polymer solution; mainly its conductivity [10]. It has been demonstrated that with addition of ionic salts, bead-less fibers with rather small diameters may be produced [7]. Though all these approaches can influence the nanofiber diameter, there are some limitations due to the presence of unwanted components, insufficient and difficult controllability, and strict thinning effect. Therefore, it is necessary to provide a method that can fabricate nanofibers with high uniformity and fineness without any additional procedures.

In recent years, centrifugal force based devices have been used to fabricate nanofibers [11-14]. Among them electro-centrifuge spinning system is an approach for manufacturing nanofibers by utilizing centrifugal force as well as electrical force, simultaneously. Although this system was initially developed for mass production of nanofibers, it suffered from a wind stream created by the rotation of the spinneret. Exposing of the ejected liquid jet to the high velocity airflow causes the jet to lose its solvent rapidly and as a consequence, the extension of the jet becomes more difficult, resulting in thicker nanofibers [12]. Therefore, further studies improved this concept using a rotating spinneret and a rotating collector. In addition, this system was securely isolated from the ambient air which introduced the air-sealed centrifuge electrospinning (ASCES) [4]. In this system we expect to be able to fabricate ultrafine nanofibers due to delayed evaporation of jet solvent resulting in more extension of the polymer jet. In the current study, we have produced solid state polymerized polyamide PA66 nanofibers via well enhanced centrifuge electrospinning by adjusting the selected affecting parameters.

It is also expected that this method would be able to fabricate polymeric particles in a large scale. Polymeric particles have been found to be useful in biomedical applications [15]. They have potentially wide range of applications in physics, chemistry, and biology such as carriers in drug delivery systems [16].

There are several methods for producing polymeric particles like solvent extraction/evaporation, spray drying, and suspension/emulsion polymerization [17].

Recently, electrospraying as a simple and cost-effective technique has been used to prepare polymeric particles

A. Valipouri and A. Hosseini are with the Department of Textile Engineering, Isfahan University of Technology, Isfahan, Iran. Correspondence should be addressed to A. Valipouri (e-mail: valipouri@cc.iut.ac.ir).

with the capability to generate size-controlled, near-monodisperse particles by optimizing the process parameters and the properties of the solution [18].

Fabrication of polymeric particles relies on electrostatic force to overcome the surface tension force and break the liquid jet into smaller particles.

In the current study we have had a preliminary study on fabricating PCL particles using ASCES.

Field-emission scanning electron microscopy (FESEM) was utilized to analyze the nanofibers as well as Poly (ε-caprolactone) (PCL) particles morphology.

II. Experimental

A. Materials

Solid state polymerized PA66 (SSP PA66) with a molecular weight of 77874 g/mol was used as received from Zanjan Tire Cord Co., Iran. Formic acid (98-100%) was purchased from Merck as a solvent of SSP PA66. Its density and boiling point were 1.22 g/mL (at 20℃) and 101℃, respectively.

Poly(ε-caprolactone) (PCL) (Mw: 80,000) and dichloromethane (DCM) were purchased from Sigma-Aldrich.

B. Preparation of Polymer Solutions

SSP PA66 was dissolved in formic acid to prepare solutions with concentrations of 12-15 wt%. All the solutions were gently stirred at room temperature for 24h to ensure homogeneity. It is worth mentioning that beaded-fibers appeared when the concentration was lower than 12 wt%.

PCL solutions with concentrations of 3 and 5 w/v % were prepared by dissolving PCL in DCM solvent. The polymer solutions were stirred magnetically for 2 h at room temperature before electrospraying.

C. Characterization

The morphology of nanofiber mats and particles was characterized using FESEM (Hitachi S-4160) instrument. Prior to observation, all the samples were coated with gold. On the FESEM images, at least 200 different points of nanofibers were randomly selected and their diameters were measured by Measurement software.

D. Air-sealed Centrifuge Electrospinning (ASCES)

As can be seen in Fig. 1, the ASCES setup consists of a rotating drive shaft (A), an insulated plate (B), a rotating cylindrical receptacle (C), a metallic cylindrical collector (D), a transparent door (E) and a high-voltage power supply (F). The rotating cylindrical receptacle holds a syringe containing a polymer solution (see Fig. 1). The polymer solution is ejected from the needle tip. The positive electrode from high-voltage power supply is connected to the nozzle, and the surrounding cylindrical collector is attached to the opposite polarity. The distances from the nozzle tip to the rotation center and to the collector are adjusted to 5.3 cm and 8 cm, respectively. The receptacle and the collector are firmly affixed to the drive shaft by an insulated plate. The movable transparent door is used to prevent air from entering and exiting. Hereafter, we call the collection of the receptacle, the nozzle, the collector, the insulated plate, and the transparent door the head of spinning or spinning head.

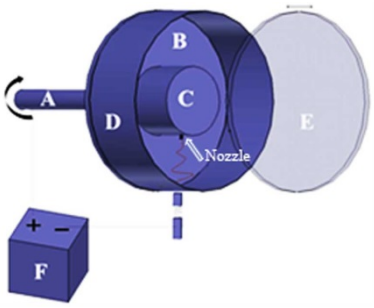

Fig. 1 A schematic of the air-sealed centrifuge electrospinning system: (A) rotating drive shaft, (B) insulated plate, (C) rotating cylindrical receptacle, (D) rotating metallic cylindrical collector, (E) transparent door (F), high-voltage power supply [4].

III. Results and Discussions

A. Nanofiber Formation and Morphology Characterization

In the air-sealed centrifuge electrospinning system, due to centrifugal force, the polymer solution governed by its surface tension is radially transported outward through the nozzle. Further increase in the rotational speed of the spinning head results in a critical value by which the centrifugal force overcomes the surface tension and a jet of the fluid is ejected from the tip of the nozzle. An electric field is applied between the nozzle containing the polymer solution and the cylindrical collector. The electric field as well as the centrifugal force direct the liquid jet toward the collector and stretch the jet to become very fine. The traveling jet solidifies through solvent evaporation and the solidified jet, turning into the nanofibre, is collected in the form of a nanofiber mat on the metallic cylindrical collector. In this study an experiment has been performed to obtain nanofibers which are as thin as possible. Fig. 2 shows the FESEM images of SSP PA66 nanofibers fabricated via ASCES by properly adjusting parameters such as solution concentration, rotational speed of spinning head, syringe content, as well as applied voltage. The process parameters, the concentration of polymer solutions and the mean and standard deviation of the diameter of four nanofiber samples are summarized in Table I. The images demonstrate that this new invention has a unique ability to produce ultrafine nanofibers just by adjusting some affecting parameters. There is no necessity for using any additive to reduce the diameter of nanofibers. This introduces a straightforward way to produce ultrafine nanofibers through air-sealed centrifuge electrospinning. As can be seen in the images, the diameter of nanofibers fabricated form solutions containing 12, 13, 14, and 15 wt% polymer is less than 100 nm. The results of our previous work [19] showed that an increase in solution concentration tends to increase the nanofiber diameter.

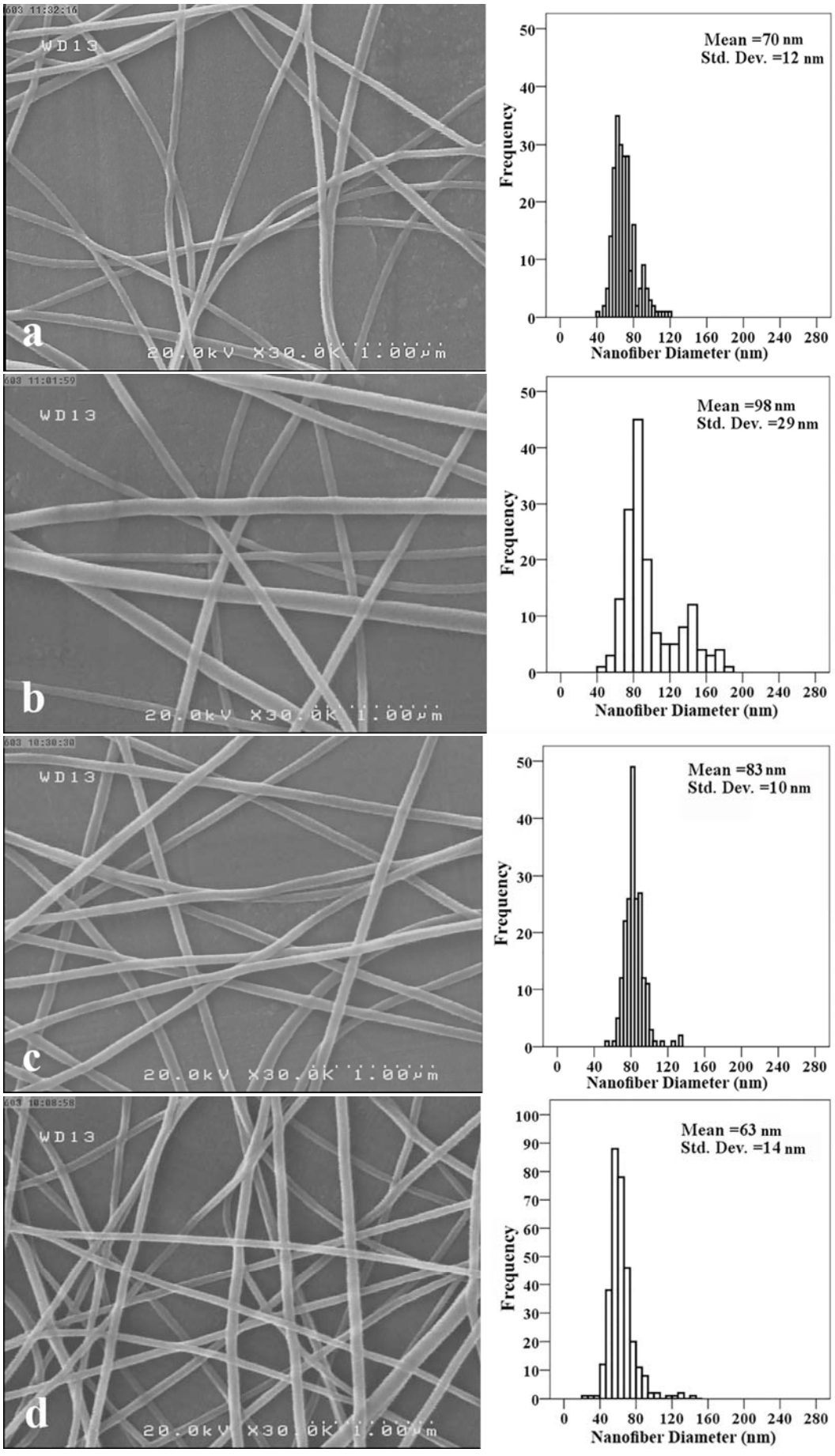

Fig. 2. FESEM images of SSP PA66 nanofibers fabricated by ASCES system: (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4.

But in our new system, with properly adjusting the process parameters, it was possible to fabricate nanofibers with diameters less than 100 nm. Also, it was found that the nanofiber diameter decreases with increasing the rotational speed. When the syringe's content was decreased, the nanofiber diameter decreased as well [19].

TABLE I
SELECTED PARAMETERS AND THEIR CORRESPONDING AVERAGE NANOFIBER DIAMETER

Sample Number		1	2	3	4
Factors	Concentration (wt%)	12	13	14	15
	Rotational speed (rpm)	1800	3240	3960	3960
	Syringe content (ml)	0.1	0.5	0.3	0.1
	Voltage (kV)	10	10	10	18
Mean diameter (nm)		70	98	83	63
Standard deviation of diameter (nm)		12	29	10	14

B. Particle Formation and Morphology Characterization

To investigate the influence of solution concentration on formation of PCL polymeric particles, two solutions of 3 and 5 w/v% PCL in DCM were electrosprayed using ASCES under conditions indicated in Table II.

Fig. 3 shows the high-magnification FESEM images of PCL particles and fibers. The FESEM images of the polymeric PCL products indicate that solution concentration has a significant influence on the microstructure of products.

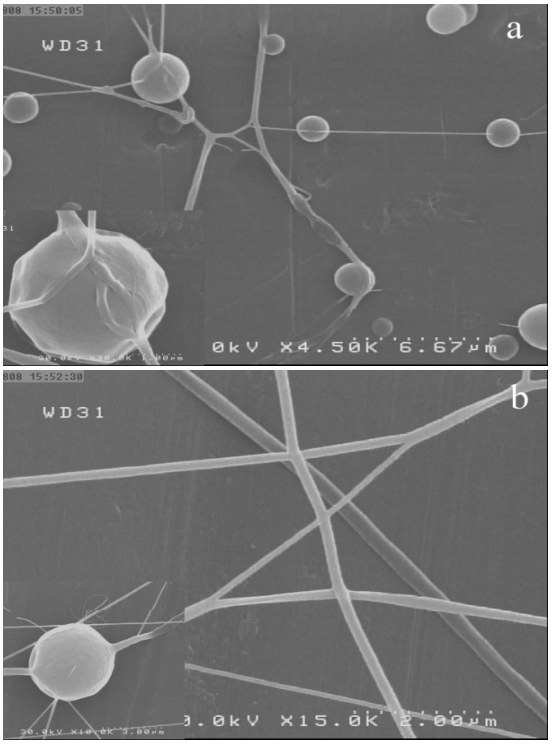

Fig.3. FESEM images of PCL polymeric products generated by (a) 3 w/v%, (b) 5 w/v%.

At 5 w/v%, a mixture of particles and fibers was produced, as shown in Fig. 3(b). When the solution concentration was decreased to 3 w/v %, the fibers disappeared, and some aggregated particles were obtained, as shown in Fig. 3(a). The morphology characteristics of the PCL products are summarized in Table II.

TABLE II
FABRICATION CONDITIONS OF PCL PRODUCTS VIA ASCES AND THEIR CORRESPONDING AVERAGE DIAMETER

Sample Number		1	2
Factors	Concentration (wt%)	3	5
	Rotational speed (rpm)	1800	1800
	Syringe's content (ml)	0.1	0.1
	Voltage (kV)	18	18
Illustratted products		particle	mixture
Mean diameter (µm)		1.62	2.4(particle)+0.0579 (fiber)
Standard deviation of diameter (µm)		0.5	0.97(particle)+0.058(fiber)

IV. CONCLUSION

We used a novel technique for producing ultrafine and high quality nanofibers by utilizing centrifugal and electrostatic forces simultaneously. The fabrication process was securely sealed from ambient airflow. The nozzle and collector rotated at the same speed. This innovative collector, nozzle, and air-sealed spinning technique could enhance the quality and fineness of nanofibers. The diameter of nanofibers could be controlled by adjusting the affecting parameters such as solution concentration, rotational speed of spinning head, syringe's content and applied voltage. Thinner fibers could be achieved by a rotational speed of 3960 rpm, a syringe content of 0.1 ml, and a voltage of 18 kV. Sample 4 had the thinnest diameter among all samples. Also this novel technique had a good ability to produce polymeric particles. The PCL particles were fabricated successfully via ASCES. By increasing the PCL solution concentration, the particles tended to disappear, and more fibers were created.

REFERENCES

[1] Z. M. Huang, Y. Z. Zhang, M. Kotaki, and S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites", *Compos, Sci. Technol.,* vol. 63, pp. 2223–2253, 2003.

[2] D Li and Y. N. Xia, "Electrospinning of nanofibers: Reinventing the wheel? ", *Adv. Mater.,* vol. 16, pp. 1151-1170, 2004.

[3] S. V. Fridrikh, J. H. Yu, M. P. Brenner, and G. C. Rutledge, "Controlling the Fiber Diameter during Electrospinning", *Phys. Rev. Lett.,* vol. 90, p. 144502, 2003.

[4] A. Valipouri, S. A. H. Ravandi, and A. Pishevar, "A novel method for manufacturing nanofibers", *Fiber. Polym.,* vol. 14, pp. 941-949, 2013.

[5] C. X. Zhang, X. Y. Yuan, L. L. Wu, Y. Han, and J. Sheng, "Study on morphology of electrospun poly(vinyl alcohol) mats", *Eur. Polym. J.,* vol. 41 pp. 423-432, 2005.

[6] W. E. Teo and S. Ramakrishna, "A review on electrospinning design and nanofibre assemblies", *Nanotechnology,* vol. 17 pp. R89–106, 2006

[7] N. Bhardwaj and S. C. Kundu, "Electrospinning: A fascinating fiber fabrication technique, " *Biotechnol. Adv.,* vol. 28 pp. 325-347, 2010.

[8] W. K. Son, J. H. Youk, T. S. Lee, and W. H. Park, "The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibers", *polymer,* vol. 45, pp. 2959–2966, 2004.

[9] T. Lin, H. Wang, H. Wang, and X. Wang, "The charge effect of cationic surfactants on the elimination of fibre beads in the electrospinning of polystyrene ", *Nanotechnology* vol. 15, p. 1375 2004.

[10] C. Huang, S. Chen, C. Lai, D. H. Reneker, H. Qiu, Y. Ye, *et al.*, "Electrospun polymer nanofibres with small diameters ", *Nanotechnology* vol. 17 pp. 1558-1563, 2006.

[11] F. Dabirian, "Experimental and Theoretical Investigation on the Nanofiber Production by Electrocentrifuge Spinning," PhD, Department of Textile Engineering, Isfahan University of Technology, 2012.

[12] F. Dabirian, S. A. H. Ravandi, and A. R. Pishevar, "Investigation of Parameters Affecting PAN Nanofiber Production Using Electrical and Centrifugal Forces as a Novel Method ", *Curr. Nanosci.,* vol. 6, pp. 545-552, 2010.

[13] M. R. Badrossamay, H. A. McIlwee, J. A. Goss, and K. K. Parker, "Nanofiber Assembly by Rotary Jet-Spinning", *Nano Lett.,* vol. 10, pp. 2257-2261, 2011/12/12.

[14] K. Sarkar, C. Gomez, S. Zambrano, M. Ramirez, E. d. Hoyos, H. Vasquez*, et al.*, "Electrospinning to forcespinning™", *Mater. Today,* vol. 13, pp. 12-14, 2010.

[15] Meng-Hua Xiong, Yan Bao, Xian-Zhu Yang, Yan-Hua Zhu, and J. Wang, "Delivery of antibiotics with polymeric particles", *Adv. Drug Deliver. Rev.,* vol. 78, pp. 63–76, 2014.

[16] Matthew A. Hood, Margherita Mari, and R. Muñoz-Espí, "Synthetic Strategies in the Preparation of Polymer/Inorganic Hybrid Nanoparticles", *Materials,* vol. 7, pp. 4057-4087, 2014.

[17] J. Siepmann, R. A. Siegel, and M. J. Rathbone, Eds., *Fundamentals and Applications of Controlled Release Drug Delivery* (Advances in Delivery Science and Technology). Springer US, 2012.

[18] A. Jaworek and A. T. Sobczyk, "Electrospraying route to nanotechnology: An overview", *J. Electrostat.,* vol. 66, pp. 197-219, 2008.

[19] A. Valipouri, S. A. H. Ravandi, and A. Pishevar, "Optimization of the Parameters Involved in Fabrication of Solid State Polymerized Polyamide (SSP PA66) Nanofibers via an Enhanced Electro-centrifuge Spinning", *J. Ind. Text.,* vol. 45, pp. 368-386, 2015.