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A Novel Needle-Less Multi-Pin-Electrospinning Method to Fabricate Nanofibers from Dilute PAN Solution

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Abstract

A novel needle-less electrospinning system, "Multi-pin-electrospinning" was developed to produce thin nanofibers from dilute Polyacrylonitrile (PAN) solutions. PAN solution was placed in an open polymer bath. 16 stainless steel pins in 4 parallel rows were attached to a metal rod to form stable polymer jets. Pins were dipped into a polymer solution by rotating the pins containing rod and under the application of the electric field, multiple Taylor cone were formed followed by the multi-jet ejection from the cone's tip, then nanofibers were deposited on the aluminum collector sheet placed above the pins. The multi-pin-electrospun nanofibers were thinner with narrower diameter distribution compared with electrospun nanofibers prepared through the conventional method. The influence of the affecting parameters such as solution concentration, applied voltage, pins-collector distance and addition of $CaCl_2$ salt on the diameter of multi-pin-electrospun nanofibers were investigated. The applied voltage change did not significantly affect the average diameter of nanofibers. At pins-collector distance of 6 cm, wet nanofibers with the beaded structure were formed, whereas on increasing the distance bundles in the fibers were disappeared and straight nanofibers with fewer beads were collected. The addition of 1 wt% $CaCl_2$ salt to the 3 wt% PAN/DMF solution resulted in the formation of smooth, almost bead-free nanofibers.

Keywords: *Needle-less electrospinning, Multi-pin, Dilute solution, Thin nanofibers, Polyacrylonitrile*.

1. INRODUCTION

Polymeric nanofibers have attracted growing interest for many momentous applications because of their wonderful properties such as high surface area per volume ratio, the capability of high porosity and high interconnectivity of pores [1]. Up to now, several methods have been used to fabricate micro or nanoscale fibers, including self-assembly [2], phase separation [3], drawing [4], template synthesis [5], electrocentrifugal spinning [6], and electrospinning [7,8]. In the self-assembly method, tiny molecules decorate themselves and build up the nanofibers. Phase separation method consists of polymer dissolution, thermally influenced gelation, solvent extraction from the gel and gel freezing followed by freeze drying. In the drawing process, polymer solution droplet is pulled into a fiber shape and then solidified by quick evaporation. Template synthesis involves the application of a nanoporous membrane for favorable material synthesis. In the electrocentrifugal spinning method, a high rate of steady dispensation stress is applied to all parts of the polymer solution. Under the applied stress, if the viscosity of the polymer is adequate, it is elongated in the shape of a string and the polymer fiber is formed after solvent evaporation. All of these approaches have their advantages and disadvantages. For example, phase separation is a time-consuming method. Drawing process can be used for individual fiber fabrication and only viscoelastic

material that can tolerate the intense deformation during the drawing can be used for nanofiber synthesis via drawing. Although template synthesis is very general and has been used for the production of nano-scale tubes and fibrils composed of a wide variety of materials such as metals and carbons, it cannot produce individual continuous nanofibers. Hence, the electrospinning method in which nanofibers are fabricated from an ejected jet of polymer solutions or melts by the application of the electric field has been shown to be the only method for individual continuous nanofibers production from a wide variety of polymers [9]. The principal concept of upscale nanofiber production is mainly based on increasing the number of needle nozzle used [10]. Although the application of multiple nozzles improves the production rate of nanofibers, there are a lot of complications such as requiring a large operating space and accurate design of the space between the needles [11]. Recently, needle-less (open solution surface) electrospinning have been developed for the production of polymer nanofibers [12]. In a typical needle-less electrospinning method, a rotational cylinder is partly immersed in a polymer solution container and a fine layer of solution is formed on the cylinder surface by the rotation of the cylinder, which is exposed to a high electric field and at a voltage higher than critical value, multi-jet are ejected [13]. Needle-less electrospinning as a new electrospinning method for production of polymer nanofibers was proposed by Yarin and Zussman who applied a high electric field to the double-layered solution including a magnetic solution as the lower layer and a polymer solution as the upper layer to generate multiple jets at the polymer solution surface [14]. Then, Niu et al. [15] employed the needle-less electrospinning with two different nozzles of a rotational disk and a cylinder. They also tested the effect of nozzle shape on the morphology of the obtained nanofibers and reported that the fibers produced by the disk were finer with narrower diameter distribution than those generated by the cylinder at the same conditions. In another attempt to improve nanofiber throughput, Liu et al. [16] used needle-disk electrospinning. However, the application of electrospun fibers is restricted by their wide diameter distribution. Fiber diameter has a significant effect on the application of nanofibers. More uniform nanofibers with a smaller diameter can be organized for applications such as tissue engineering, artificial cornea and filtration [17, 18]. Nowadays, there is a growing demand for polymer fiber diameter reduction to 10 nm and lower for wide applications including nano-sized reinforcement, tissue engineering, a template for hollow fiber with nano-sized inner diameters and others [19]. The morphology of the electrospun nanofibers is affected by several parameters including solution properties (e.g. concentration and conductivity), process parameters (e.g. applied voltage and tip to collector distance) and parameters of surrounding condition (e.g. relative humidity) [20]. For instance, Baumgarten [21] reported that the average diameter of fibers was increased by increasing the solution viscosity (an increase in the solution concentration). Mit-uppatham et al. [20] added some inorganic salts to the spinning solution and found that the addition of salts increased the conductivity of polymer solution and resulted in the fiber diameter increase. This study reports the production of polyacrylonitrile nanofibers fabricated from dilute solution through the multi-pin-electrospinning method for the first time. The nanofiber diameters of the multi-pin-electrospun nanofibers were lower than those of the nanofibers prepared by electrospinning. The influence of the affecting parameters such as solution concentration, applied voltage, pins-collector distance and addition of $CaCl_2$

salt on the diameter of multi-pin-electrospun nanofibers were investigated.

2. MATERIALS AND METHODS

2.1. Materials

Industrial Polyacrylonitrile (PAN) with a number average molecular weight ($\overline{M_n}$) of 70000 g/moL was received from Iran Polyacryle Co. and N, N-Dimethyl-flormamide (DMF) was purchased from Merck. Calcium chloride ($CaCl_2$) which was used as an additive to the dilute PAN solution was purchased from Merck.

2.2. Sample Preparation

The electrospinning system, in its conventional form, consists of a syringe as a polymer solution or melt container, a needle, a collector, and the DC voltage power supply. In the electrospinning process, an electric field is applied between the hemispherical droplet of polymer solution suspended at the needle tip and a collector. The droplet surface is distorted into the well-known Taylor cone through electrostatic charging due to its surface charge repulsion. Then, charge repulsion overcomes the surface tension of the polymer drop at the cone tip and a jet of the charged polymer solution is ejected towards the collector. During the jet traveling towards the collector, the jet undergoes bending instabilities and traces a curved and spiral line which elongates the jet and decreases the fiber diameter considerably. Finally, the solvent evaporates and continuous polymer nanofibers are deposited randomly on the collector surface [22,23]. In our multi-pin-electrospinning setup, as shown in Figure 1, there was no syringe and needle, and the spinning solution was placed in an open polymer bath. 16 stainless steel pins in 4 parallel rows were attached to a metal rod to form stable polymer jets as shown in Figure 1. The aluminum sheet was placed over multi-pin system used as a collector, the distance between the pins tip and the collector sheet was adjustable. Pins were dipped into a polymer solution by rotating the pins containing rod; the thin layer of polymer covered the surface and tips of the pins due to the surface tension of the solution, so a hemispherical droplet was formed at the tip of each pin. The process was driven by an electrical potential, which was applied between the multi-pin and a collector sheet. The applied voltage induced a high electric charge on the surface of a drop at each pin tip and distorted the hemispherical shape of each drop into the conical shape. Eventually, the electrostatic forces in the droplets overcame the surface tension of the drops by an additional increase in the electrical field and multi-jet ejected from the multi-pin tip. After the ejection of the jet, they were elongated and the solvent was evaporated and nanofibers were deposited on the aluminum collector sheet placed above the pins. To investigate the effect of concentration, applied voltage, pins-collector distance and addition of $CaCl_2$ and also to compare the properties of the two types of fibers produced through electrospinning and multi-pin-electrospinning, PAN solutions were prepared in different concentrations ranging from 3 to 15 wt% under vigorous stirring for 24 h. All the electrospinning experiments were performed for 3 minutes at room temperature.

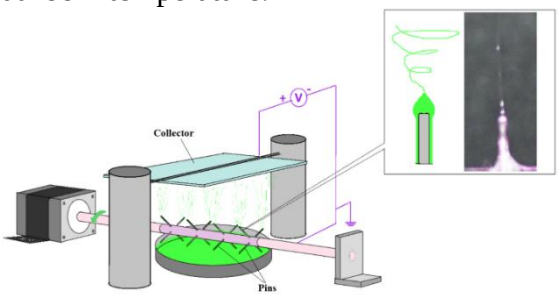

Figure 1. *The schematic of multi-pin-electrospinning setup and the image of initiating stable polymer jets from pins.*

2.3. Characterization

The prepared fibrous samples were characterized using a scanning electron microscope (FESEM, TSCAN, Czech Republic). The ImageJ software was used to quantify the fibers' diameters from SEM

micrographs. Microsoft Excel was used to calculate the average fiber diameter and its standard deviation. To investigate the effect of concentration, applied voltage and pins-collector distance on nanofiber diameters, the diameters data were analyzed by one-way ANOVA using IBM SPSS statistics 23 software.

3. RESULTS AND DISCUSSION

3.1. Comparison of Fiber Properties Obtained Through Electrospinning and Multi-Pin-Electrospinning Methods

To fabricate fibers by electrospinning, an appropriate polymer concentration is required, lower than which, the ejected liquid jet breaks down into droplets due to insufficient polymer chain entanglement to prevent the collapse of the jet [24]. In this study, PAN nanofibers from dilute solution with the concentration of 3 wt% PAN in DMF were successfully prepared by multi-pin-electrospinning method, whereas, using conventional electrospinning at the PAN solution with the concentration of 8 wt% and lower, regardless of applied voltage, due to inadequate polymer chain entanglement for jet stabilization, droplets rather than fibers were formed on the collector [25]. It should be noted that, in this method (multi-pin-electrospinning) owing to the lower diameter of the produced nanofibers, the volume of nanofiber production is lower than the conventional electrospinning method. Figure 2 shows the SEM images of both electrospun and multi-pin-electrospun PAN fibers from solutions with different concentrations of 8, 9 and 13 wt%. Droplets (Figure 2(a)) and fibers with beaded structures (Figure 2(c)) were formed through the electrospinning method from PAN solution with the concentration of 8 and 9 wt%, respectively. However, at the same concentrations of the PAN solutions, uniform nanofiber structures with a smooth surface were prepared through the multi-pin-electrospinning method (Figure 2(b,d)). Furthermore, the average fiber diameter of multi-pin-electrospun nanofibers was lower than that of electrospun nanofibers. For instance, the average fiber diameter at PAN solution with the concentration of 13 wt% for fiber prepared by electrospinning was 337.23±26.5 nm, while it was 205.69±34.8 nm for the fibers prepared by multi-pin-electrospinning at the same concentration (Figure 2(e,f)).

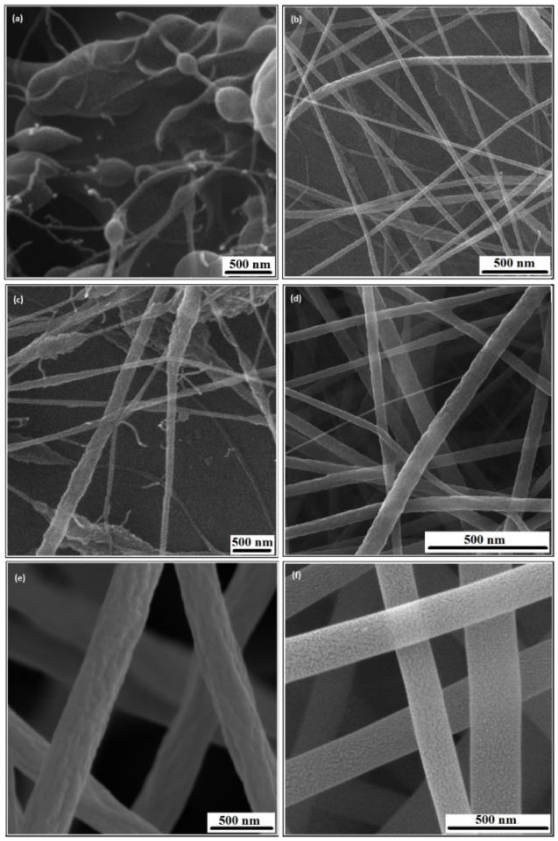

Figure 2. *The SEM images of electrospun PAN fibers from polymer solutions with the concentrations of a) 8 wt%, c) 9 wt% , and e) 13 wt% (applied voltage of 22 kV and pins-collector distance of 12 cm) and multi-pin-electrospun PAN fibers from various polymer solutions with the concentrations of b) 8 wt%, d) 9 wt%, and f) 13 wt% (applied voltage of 22 kV and pins-collector distance of 12 cm).*

3.2. Effect of Concentration

Polymer concentration is generally considered as the most suitable parameter to adjust the required morphology and diameter [26]. A series of experiments from PAN solutions with different concentrations of 3, 6 and 9 wt% were

performed under the same operating condition and the results for the diameter of the fibers were studied by one-way ANOVA analysis. The SEM images and the corresponding frequency distribution of nanofiber diameters at different PAN concentrations are shown in Figure 3.

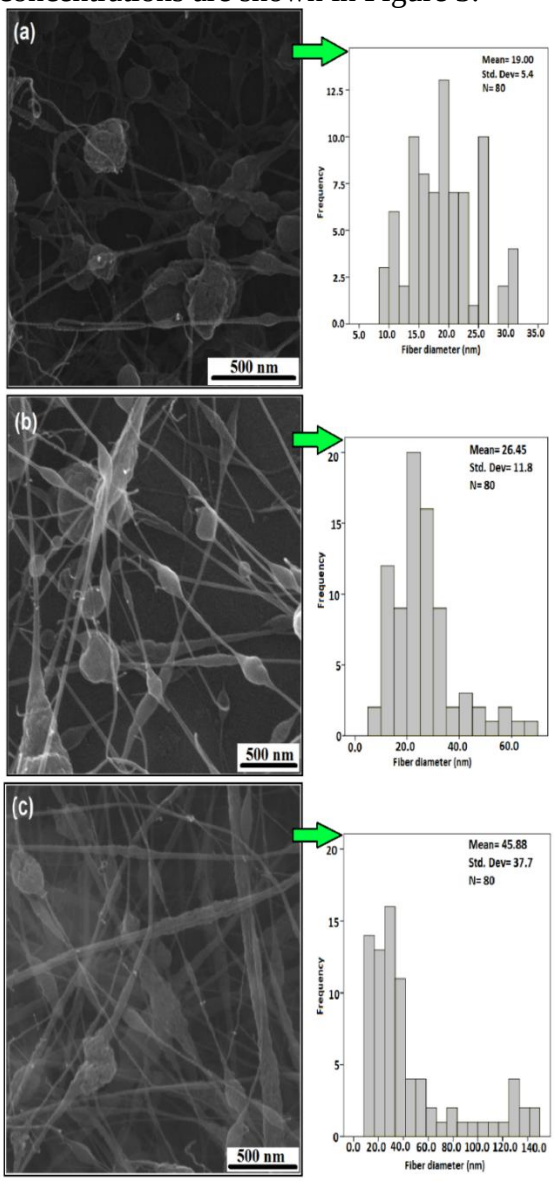

Figure 3. *The SEM images of nanofibers and corresponding frequency distribution of nanofiber diameters produced at pins-collector distance of 6 cm and applied voltage of 22 kV from PAN solutions with the concentrations of (a) 3 wt%; (b) 6 wt%; (c) 9 wt%.*

At 3 wt% PAN/DMF, beaded nanofibers were formed with narrow fiber diameter distribution with an average diameter of 19.00±5.4 nm. As the concentration of the polymer solution increased to 6 wt%, the average nanofibers diameter increased to 26.45±11.8 nm. More smooth nanofibers with broader fiber diameter distribution with an average diameter of 45.88±37.7 nm were obtained at a PAN solution with the concentration of 9 wt%. Similar results of polymer concentration effects on diameter and fiber morphology were reported previously [27,28]. As shown in Table 1, the ANOVA results revealed that the polymer concentration affected the average diameter of multi-pin-electrospun PAN nanofibers produced by our multi-pin-electrospinning significantly at $p<0.05$. To compare the diameter of multi-pin-electrospun PAN nanofibers at different polymer concentrations, Tukey's posthoc analysis was used. As shown in Table 2, the nanofiber diameter increased significantly by polymer concentration increase from 3 and 6 to 9 wt%. In other word, in multi-pin-electrospinning like other electrospinning systems, the average fiber diameter increased with polymer concentration increase. Our results also revealed that the shape of beads was strongly affected by polymer concentration; The beads formed along the fibers changed from hemispherical shape to spindle-like with increasing the polymer concentration.

Table 1. *The ANOVA results of nanofiber diameters at different polymer concentrations.*

	Sum of Squares	df	Mean Square	*F*	*Sig.*
Between Groups	30797.7	*2*	15398.8	28.9	0.0
Within Groups	126099.3	*237*	532.0		
Total	156897.0	*239*			

3.3. Effect of Voltage

In electrospinning, the electric current of the ionic conduction of charges within the

polymer solution is very small that is presumed insignificant, so the flow of the ejected polymer from the tip to collector distance is merely responsible for charge transport and the spinning electric current is increased with increasing the applied voltage [29].

Table 2. *The Tukey's posthoc comparison of nanofiber diameters at polymer solutions with the concentrations (C) of 3, 6, and 9 wt% (voltage of 22 kV and pins-collector distance of 6 cm).*

C		Mean Difference	Std. Error	Sig.	L. Bound	U. Bound
3	6	-7.4	3.6	0.105	-16.0	1.1
	9	-26.8	364.7	0.000	-35.4	-18.2
6	3	7.4	3.6	0.105	-1.1	16.0
	9	-19.4	3.6	0.000	-28.0	-10.8
9	3	2687087	3.6	0.000	18.2	35.4
	6	19.4	36	0.000	10.8	28.0

In these experiments for 3 wt% PAN in DMF solution, at 15 kV, initiation of the jets did not occur. As the voltage increased to 16 kV the electrospinning jets initiated from the stable cones at pins surface and tip. Hence, the initiation of jets for PAN/DMF at each pins-collector distance was strongly affected by voltage. For 3 wt% PAN/DMF, at distances of 6, 8, 10, 12, and 13 cm initiation of the jets occurred at voltages of 16, 16, 19, 19, and 22 kV, respectively. A series of tests were done at different voltages from 16 to 22 kV at a polymer solution with a concentration of 3 wt%, and pins-collector distance of 6 cm. Figure 4 shows the SEM images of nanofibers and frequency distribution of nanofiber diameters indicating that thin nanofibers with diameters lower than 22 nm were collected on the collector at all applied voltages. It is clear from Figure 4 that the applied voltage change did not significantly affect the average diameter of the obtained multi-pin-spun nanofibers. The ANOVA analysis with 95% confidence limit also confirmed the obtained results (Table 3). The similar behavior of no significant effect of applied voltage on the average diameter of electrospun PAN fibers was reported previously [30].

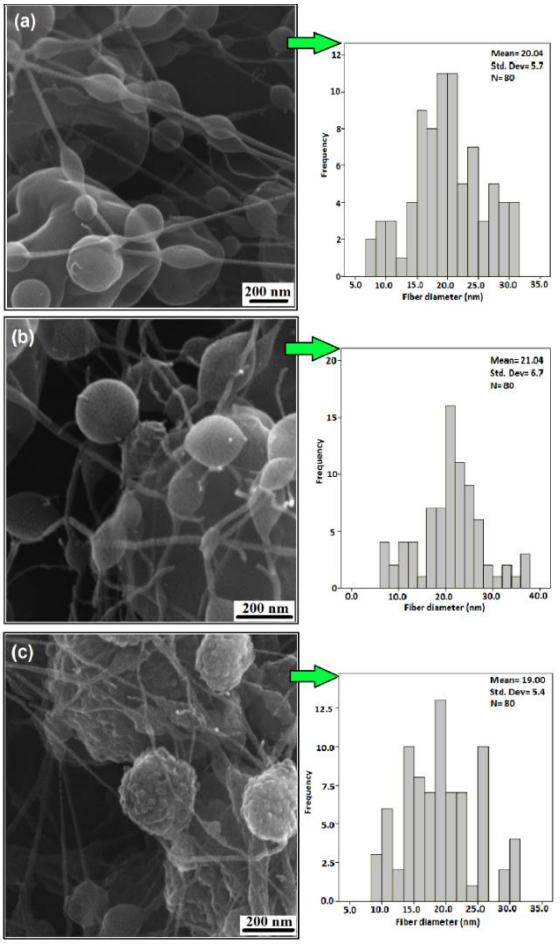

Figure 4. *The SEM images of nanofibers and corresponding frequency distribution of nanofiber diameters produced from a 3 wt% PAN/DMF at pins-collector distance of 6 cm and voltages of (a) 16 kV; (b) 19 kV; and (c) 22 kV.*

3.4. Effect of Distance

Tip to collector distance is one of the essential parameters that affects the structure and morphology of the fibers fabricated by electrospinning due to its effects on fiber collecting time,

evaporation amount and instability and whipping during the jet traveling [29].

Table 3. *The ANOVA results of nanofiber diameter at different applied voltages.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	165.4	2	82.7	2.2	0.1
Within Groups	8653.1	237	36.5		
Total	8818.5	239			

In this study, the structure of multi-pin-electrospun PAN nanofibers was examined with pins-collector distance variation from 6 to 10 cm at PAN solution with the concentration of 3 wt% and an applied voltage of 19 kV. As shown in Figure 5, at a pins-collector distance of 6 cm, wet nanofibers with beaded structure as well as bundles in the nanofibers were deposited on the collector. As the pins-collector distance was increased, bundles were disappeared and straight nanofibers with fewer beads were collected due to the sufficient evaporation of DMF from ejected jets during the jets traveling. The effect of pins-collector distance on nanofiber diameter was also assessed by ANOVA followed by Tukey's posthoc analysis. The ANOVA results indicated that the multi-pin-electrospun fiber diameters had changed significantly by pins-collector distance at the $p<0.05$ level (Table 4). Tukey's posthoc comparison, as shown in Table 5 shows that the pins-collector distance change from 6 to 8 cm and 8 to 10 cm had no significant effect on average nanofiber diameter of multi-pin-electrospun nanofibers.

However, the average diameter of multi-pin-electrospun nanofibers at a pins-collector distance of 10 cm was significantly thinner than where the pins-collector distance of 6 cm. The average multi-pin-electrospun nanofiber diameter was decreased from 21.04±6.7 nm to 20.16±13.8 and 17.20±6.7 nm when the pins-collector distance was increased from 6 cm to 8 and 10 cm, respectively (Figure 5).

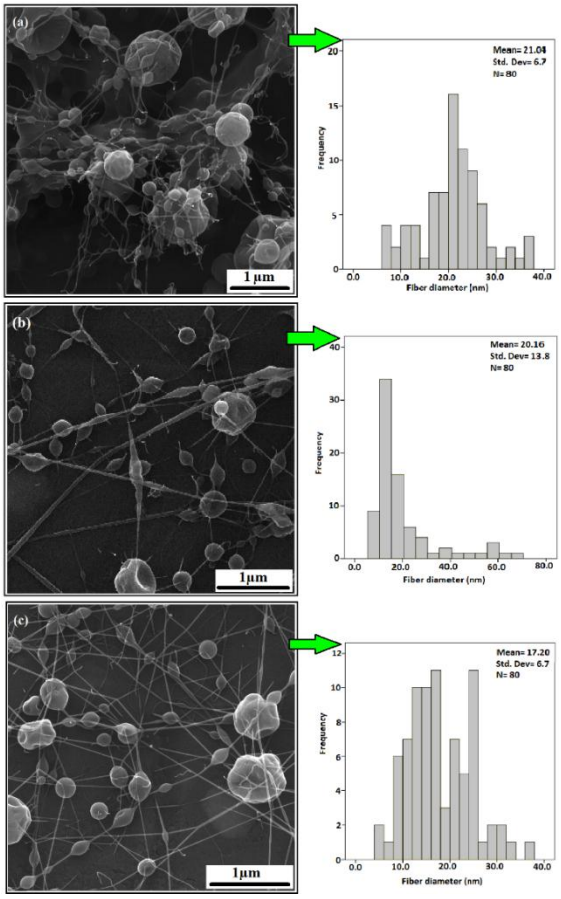

Figure 5. *SEM images of multi-pin-electrospun PAN nanofibers (concentration of 3 wt%, voltage of 19 kV), pins-collector distances of (a) 6 cm; (b) 8 cm, and (c) 10 cm.*

Table 4. *The ANOVA results of nanofiber diameter at different pins-collector distances.*

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	647.4	2	323.7	3.4	0.03
Within Groups	22451.3	237	94.7		
Total	23098.7	239			

Table 5. *The Tukey's posthoc comparison of nanofiber diameter at pins-collector distance (D) of 6, 8, and 10 cm (concentration of 3 wt% and voltage of 19 kV).*

D		Mean Difference	Std. Error	Sig.	L. Bound	U. Bound
6	8	0.87	1.5	0.837	-2.7	4.5
	10	3.83	1.5	0.035	0.2	7.4
8	6	-0.87	1.5	0.837	-4.5	2.7
	10	2.96	1.5	0.134	-0.6	6.5
10	6	-3.83	1.5	0.035	-7.4	-0.2
	8	-2.96	1.5	0.134	-6.5	0.6

3.5. Effect of Salt

The nanofiber morphology in the electrospinning technique is affected by surface tension because of the fact that for jet initiation, the electrical force ought to be high enough to overcome the surface tension of the polymer solution. At low surface tension in which the concentration of solvent is high, solvent molecules try to minimize the specific surface area of the polymer solution by congregation into a spherical-like shape. However, at a higher viscosity of polymer due to the greater mutual influences between the solvent and polymer, the solvent molecules diffuse into the polymer chains under the electrical field. Hence, the surface tension is suppressed and the smooth fibers are produced [31, 32]. It had been reported earlier that the viscosity of PAN solution increased by the addition of inorganic salts when the concentration of PAN is low [33]. Therefore, in this study, to prevent the formation of beaded fibers, 1 wt% $CaCl_2$ salt was added to a 3 wt% PAN/DMF solution and smooth, almost bead-free PAN multi-pin-electrospun nanofibers with the average diameter of 26.18±14.3 nm were obtained successfully as shown in Figure 6.

3.6. The Mathematical Model for Nanofiber Diameter

In order to find the relation between nanofiber diameter and solution concentration in needle-less electro-spinning, the following mathematical model was suggested before [34]. At solution concentration lower than a threshold value, the relation between nanofiber diameter and solution concentration is as follows:

$$d = k_1 + k_2C + k_3C^2 + k_4C^3 + \alpha(C) \quad (1)$$

where d is nanofiber diameter, k_i are model constants, c is solution concentration, and α(c) is a matching term for concentrations lower than the threshold value.

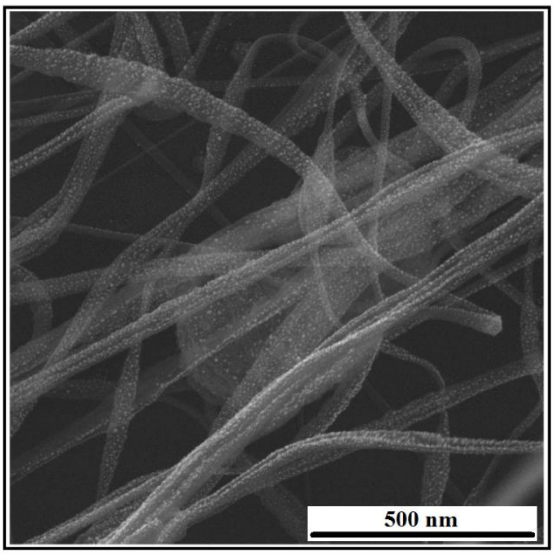

Figure 6. *SEM image of multi-pin-electrospun PAN nanofibers from 3 wt% PAN/DMF solution + 1 wt% $CaCl_2$ salt (voltage of 16 kV and pins-collector distance of 8 cm).*

And for solution concentration higher than the threshold value, the relation between nanofiber diameter and solution concentration is as follows:

$$d = 1/b_1 + b_2C + b_3C^2 + b_4C^3 + \beta(C) \quad (2)$$

where d is nanofiber diameter, b_i are model constants, c is solution concentration, and β(c) is a matching term for concentrations higher than a threshold value.

If the above equations are combined, the following equation is used to find the relation between nanofiber diameter and solution concentration.

$$d = k_1 + k_2C + k_3C^2 + k_4C^3 + 1/(b_1 + b_2C + b_3C^2 + b_4C^3) \quad (3)$$

For our prepared needle-less multi-pin electrospinning the constants of the Eq. (3) were obtained as follows:

k_1=2.70, k_2=9.12, k_3=-1.77, k_4=0.14, b_1=-3.64, b_2=2.85, b_3=-0.52, b_4=0.003

and then the Eq. (3) for the present study was obtained as follows:

$$d = 2.70 + 9.12C - 1.77C^2 + 0.14C^3 + 1/(-3.64 + 2.85C - 0.52C^2 + 0.003C^3)$$

4. CONCLUSION

Thin nanofibers were successfully prepared from dilute PAN solutions by a newly developed needle-less multi-pin electrospinning method, which opens up opportunities for enhancing the quality of thin nanofibers from dilute solutions. The multi-pin-electrospun nanofibers had considerably lower fiber diameter compared to electrospun fibers prepared through the conventional method. The average fiber diameter obtained through electrospinning from the PAN solution with the concentration of 13 wt% was 337.23±26.5 nm, while it was 205.69±34.8 nm in the case of fibers prepared by pin-electrospinning. The nanofiber diameter increased significantly by polymer concentration increase from 3 and 6wt% to 9 wt%. In the needle-less electrospinning like other electrospinning systems, the average fiber diameter increased with polymer concentration increase. The results obtained revealed that the applied voltage change did not significantly affect the average diameter of multi-pin-electrospun nanofibers. The average diameter of multi-pin-electrospun nanofiber at concentration of 3 wt% and applied voltage of 19 kV, was decreased from 21.04±6.7 nm to 20.16±13.8 and 17.20±6.7 nm when the pins-collector distance was increased from 6 cm to 8 and 10 cm, respectively. To prevent the formation of beaded fibers, 1 wt% $CaCl_2$ salt was added to a 3 wt% PAN/DMF solution and smooth, almost bead-free PAN multi-pin-electrospun nanofibers successfully were obtained.

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