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Effects of Process and Ambient Parameters on Diameter and Morphology of Electrospun Polyacrylonitrile Nanofibers[1]

Seyed Mahdi Seyed Shahabadi*, Amanj Kheradmand, Vahab Montazeri, and Hossein Ziaee

Young Researchers and Elites Club, North Tehran branch, Islamic Azad University, Tehran, P.O.Box:11365-11155, Iran

**e-mail: mehdi.shahabadi7@gmail.com*

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Abstract—The diameter of the nanofibers produced by electrospinning is a key parameter for their potential applications. In this study, electrospinning was used to produce polyacrylonitrile (PAN) nanofibers at varying parameters of solution concentration, applied voltage, spinning distance, surroundings temperature, and needle diameter. To investigate the effects of these parameters on the fiber morphology and diameter, wide range of them were selected and 24 systematic experiments were carried out. The results revealed that the solution concentration had a significant influence on both morphology and diameter of the nanofibers. With increasing solution concentration from 7 to 19 wt %, the morphology was changed from beaded fibers to uniform fibers and the fiber diameter noticeably increased, ranging from 84 to 757 nm. In addition, solution properties such as viscosity and surface tension at different concentrations were measured for a thorough examination of the solution concentration effect. Also, increasing applied voltage and spinning distance resulted in a minimum in fiber diameter. Moreover, the diameter of nanofibers decreased with an increase and a decrease in surroundings temperature and needle diameter, respectively. Optimum conditions for fabricating nanofibers with minimum diameter and best morphology were determined and PAN nanofibers with diameter of 88 nm were produced.

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INTRODUCTION

Electrospinning is one of the processing approaches to make polymer fibers with diameter in the range of a few nanometers to a few microns. This approach has gained rapid interest and attention in recent years due to its versatility and potential applications in diverse fields [1]. Electrospun nanofibers have several remarkable characteristics such as high aspect ratio, porosity, and special chemical and physical properties which make them excellent candidates for filtration, drug delivery carrier, tissue engineering scaffold, and wound healing [2–9]. In electrospinning, usually a

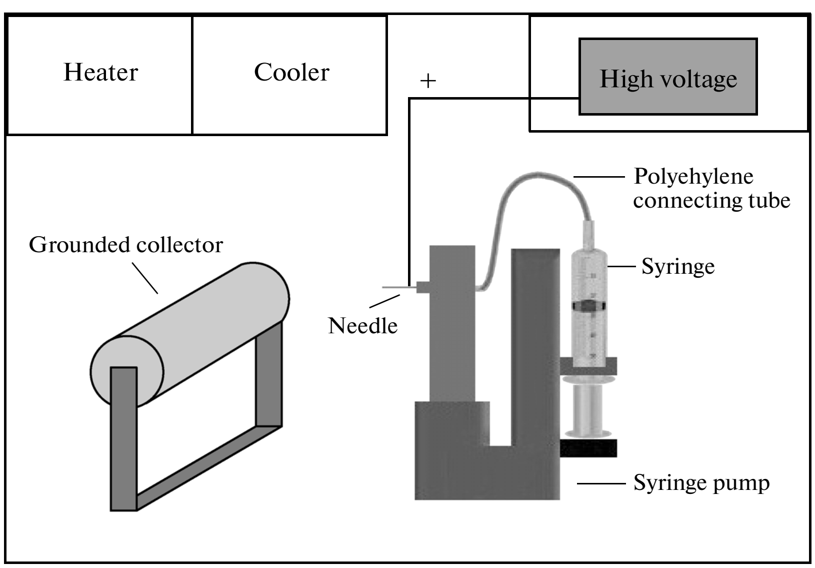

Fig. 1. Schematic diagram of electrospinning setup.

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Table 1. Design matrix of the systematical experiments

Run	Solution concentration, wt %	Applied voltage, kV	Spinning distance, cm	Temperature, °C	Needle gauge number
1	7	20	15	30	20
2	10	20	15	30	20
3	13	20	15	30	20
4	16	20	15	30	20
5	19	20	15	30	20
6	13	15	15	30	20
7	13	20	15	30	20
8	13	25	15	30	20
9	13	30	15	30	20
10	13	35	15	30	20
11	13	20	10	30	20
12	13	20	15	30	20
13	13	20	20	30	20
14	13	20	25	30	20
15	13	20	15	30	20
16	10	20	15	15	20
17	10	20	15	20	20
18	10	20	15	25	20
19	10	20	15	30	20
20	10	20	15	30	16
21	10	20	15	30	17
22	10	20	15	30	18
23	10	20	15	30	19
24	10	20	15	30	20

polymer solution is subjected to a very high electrostatic force which causes the polymer drop from the tip of the needle connected to the syringe be deformed into a conical shape (Taylor cone). When the applied voltage crosses a threshold value at which electrostatic forces overcome the surface tension, a fine charged jet is ejected from the Taylor cone. As the electrified jet travels through the air, the solvent evaporates while the polymer fiber is stretched, elongated, whipped, and finally deposited on the grounded collector as a random electrospun nanofibrous mat.

Despite the apparent simplicity of the electrospinning principle, the process itself is quite complicated because many parameters influence the properties of the obtained nanofibrous structures. Previous studies indicate that the development of useful applications of electrospun nanofibers requires a thorough understanding of the electrospinning parameters as the morphology and diameter of the electrospun nanofiber will have an influence on the final product [10]. The diameter and morphology of the nanofibers affect mechanical, electrical, and optical properties of resultant nanofibers. It has been shown that fiber diameter affects the mean and maximum pore size, pore size distribution, porosity, conductivity, mechanical strength, and water contact angle of the electrospun nanofibrous mats [11–14]. The parameters affecting diameter and mor-

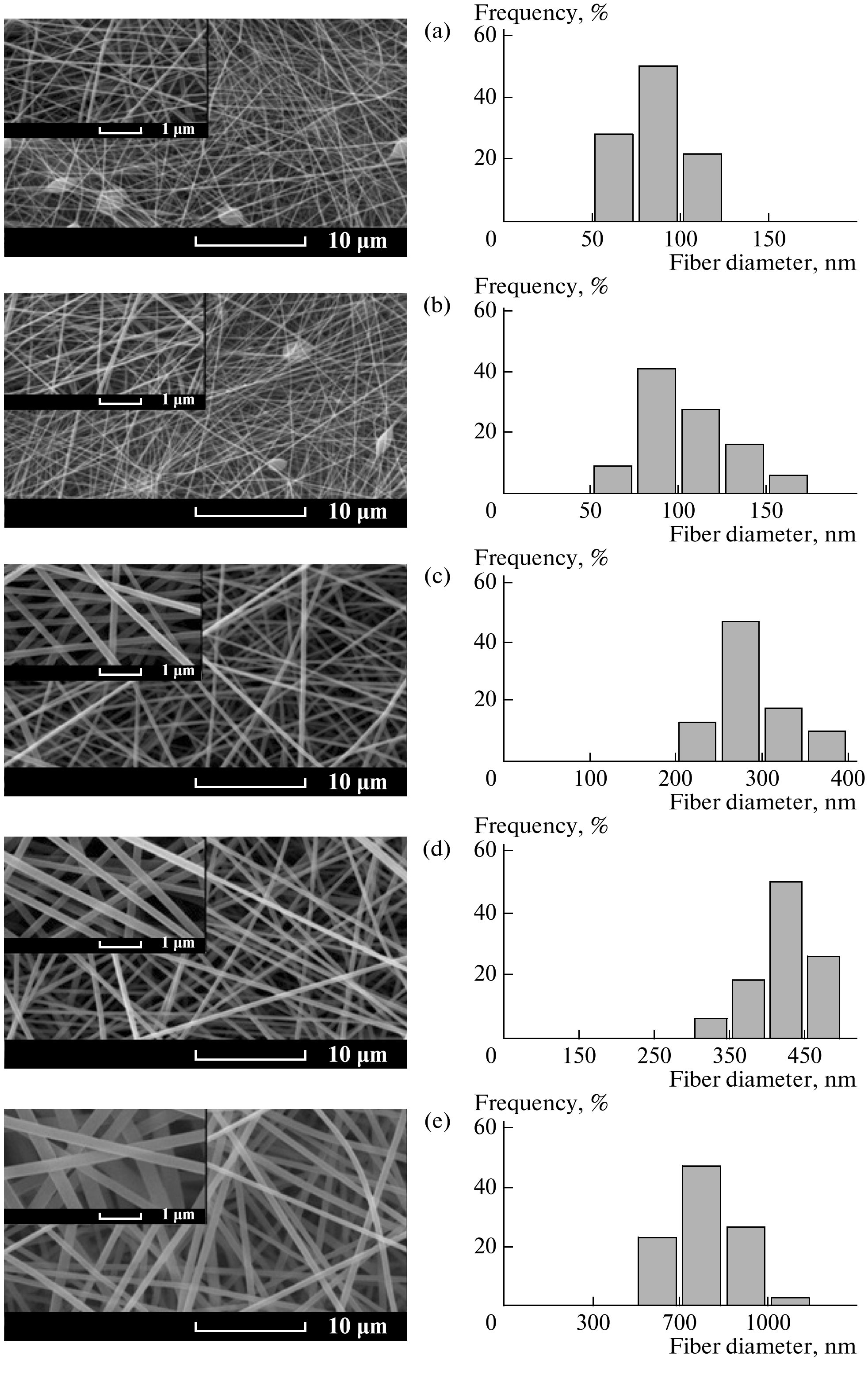

Fig. 2. SEM micrographs and diameter distribution of PAN fibers at various solution concentrations: (a) 7, (b) 10, (c) 13, (d) 16, and (e) 19 wt % (applied voltage: 20 kV; spinning distance: 15 cm; $T = 30°C$; needle gauge number: 20). The insets show higher magnification images.

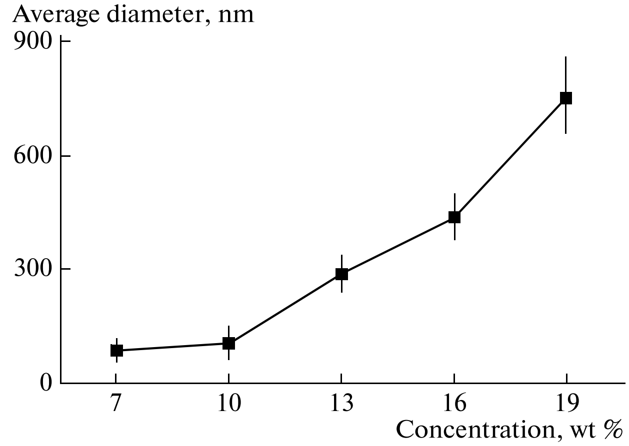

Fig. 3. Average diameters of electrospun PAN fibers at various solution concentrations (applied voltage: 20 kV; spinning distance: 15 cm; $T = 30°C$; needle gauge number: 20).

phology of the nanofibers in electrospinning process may be classified widely into solution, process, and ambient parameters. Solution parameters include viscosity, molecular weight, conductivity, and surface tension; whereas process parameters include applied voltage, tip to collector distance, flow rate, type of collector, and diameter of needle. In addition to these variables, ambient parameters encompass the humidity and temperature of the surroundings. Several studies have been performed in electrospinning process to study the effects of some of these parameters on fiber morphology [10, 15, 16].

In the present work, polyacrylonitrile (PAN) dissolved in *N*,*N*-dimethylformamide (DMF) solution was electrospun under various conditions. The influence of five important electrospinning parameters on the morphology and diameter of electrospun PAN nanofibers was investigated. Parameters studied are solution concentration, applied voltage, tip to collector distance (spinning distance), surroundings temperature, and needle diameter. The attention about the effects of surroundings temperature and needle diameter on morphology of electrospun nanofibers was not paid enough, and their relationships were discussed in detail in this work.

EXPERIMENTAL

Preparation of Polymer Solution

PAN (with average molecular weight of 100 000 g/mol) was purchased from Polyacryle Co. (Iran).DMF was used as PAN solvent which obtained from Merck Co. (Germany). Homogeneous solutions with different concentrations ranged from 7 to 19 wt % were prepared by stirring PAN powder in DMF for 16–24 hours at 60°C.

Electrospinning

Electrospinning was conducted in an electrospinning unit (ES1000, Fnavarannano-meghyas Co., Iran). The schematic diagram of the process is shown in Fig. 1. A high voltage DC power supply was used to produce the voltages ranging from 15 to 35 kV and also the spinning distance was varied from 10 to 25 cm. The polymer solution was placed in a 10 ml plastic syringe and a syringe pump was used to feed the polymer solution into the needle tip at a rate of 1 ml/h. A heater and a cooling system were used to control surroundings temperature from 25 to 40°C. Also, two fans were used to control overheating and discharging solvent vapor. Five different blunt needles with 16, 17, 18, 19,

Table 2. PAN/DMF solution properties

Concentration, %	Viscosity, mPas	Surface tension, mN/m
7	575.2	37.86
10	694.5	38.63
13	852.5	39.26
16	1078.4	40.08
19	1342.3	40.81

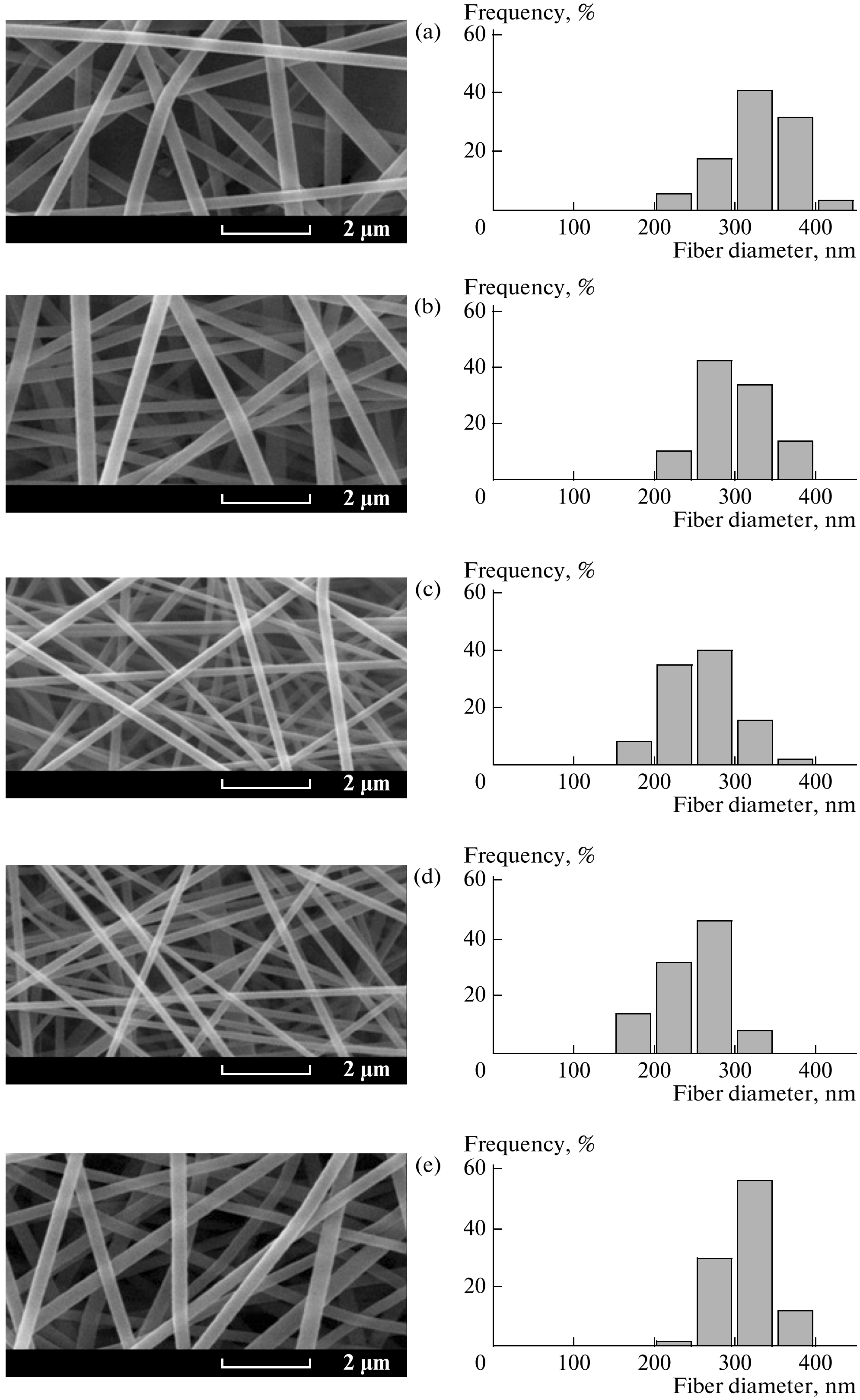

Fig. 4. SEM micrographs and diameter distribution of the PAN nanofibers at different applied voltages: (a) 15, (b) 20, (c) 25, (d) 30, and (e) 35 kV (solution concentration: 13 wt %; spinning distance: 15 cm; $T = 30°C$; needle gauge number: 20).

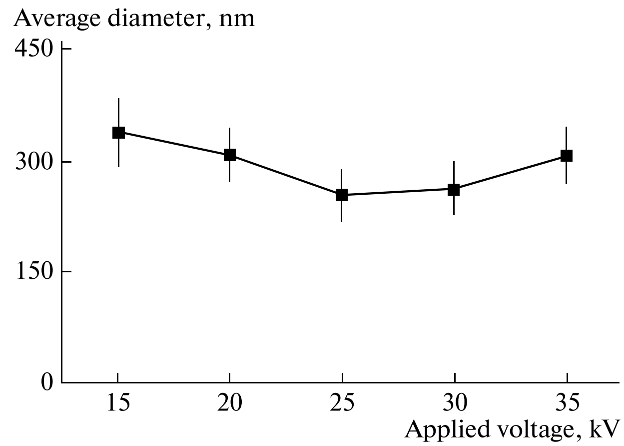

Fig. 5. Influence of applied voltage on average diameter of electrospun PAN nanofibers (solution concentration: 13 wt %; spinning distance: 15 cm; $T = 30°C$; needle gauge number: 20).

20 gauge numbers (1.19, 1.07, 0.84, 0.69, and 0.60 mm inner diameter, respectively) were used as the spinneret and the spinneret speed was fixed at 10 mm/s. The rotating drum was covered with aluminum foil, and the rotating speed was fixed at 300 rpm.

In order to investigate the effects of solution concentration, applied voltage, spinning distance, surroundings temperature, and needle diameter on fiber morphology and diameter, 24 systematic experiments were carried out. Table 1 shows these experiments.

Measurements

Morphological observation of the electrospun nanofibers was performed by scanning electron microscopy (SEM) from Philips Co. (Holland) at an accelerating voltage of 25 kV after being gold-coated. Nanofibers diameter was determined by ImageJ software (http://rsb.info.nih.gov/ij/) from averaging at least 40 randomly selected fibers of SEM images. Viscosity and surface tension of the solutions were determined by dynamic shear rheometer (Anton Paar CTD450, Austria) and surface tension meter (KSV sigma 700, Finland), respectively.

RESULTS AND DISCUSSION

Effect of Polymer Solution Concentration

Previous studies have reported that the concentration of polymer solution is the most effective parameter on bead formation and diameter of the fibers [10, 15, 17]. To investigate the effect of solution concentration on the diameter and morphology of nanofibers, PAN solutions were prepared from 7 to 19 wt % by 3 wt % intervals. SEM micrographs and size distribution of PAN nanofibers in this study are shown in Fig. 2. As shown in Fig. 2, with increasing solution concentration, the morphology was changed from beaded fibers to uniform fibers structure. In fact, bead formation, which is the product of jet instabilities under an electric field, is affected by several factors such as polymer concentration, viscosity, and surface tension of the solution. Table 2 shows the solution properties, i.e., viscosity and surface tension of the solution. It can be seen from Table 2 that both the viscosity and surface tension of these solutions increased with increasing solution concentration, although the relationship between concentration and viscosity is much stronger than the relationship between concentration and surface tension of the solution. In particular, the viscosity had a profound effect on the electrospinning process and the resulting fiber morphology. When the viscosity was too low, e.g. 7 wt %, there were numerous beads dispersed on the fibers (Fig. 2a). The reason why beads are formed at lower solution concentration is that at lower viscosity, the higher amount of solvent molecules and fewer chain entanglements mean that surface tension has a dominant effect along the electrospinning jet causing beads to form along the fibers [18]. On the other hand, at higher viscosity, due to higher amount of polymer chains entanglement in the solution, the charges on the electrospinning jet are able to fully stretch the solution with the solvent molecules distributed among the polymer chains resulting in formation of bead-free nanofibers, as shown in Fig. 2. Thereby, it can be said that a minimum solution concentration is needed to produce bead-free, uniform nanofibers for each polymer, which in case of PAN nanofibers this critical concentration is 10 wt % according to Fig. 2.

According to Fig. 2 with increasing concentration, the diameter distribution became wider. The increased macromolecular chain entanglements as a result of increasing the polymer concentration, causes more difficulty for the jet to stretch and split, and consequently, results in less uniform fibers and wider diameter distribution [19]. Moreover, Figure 3 shows the

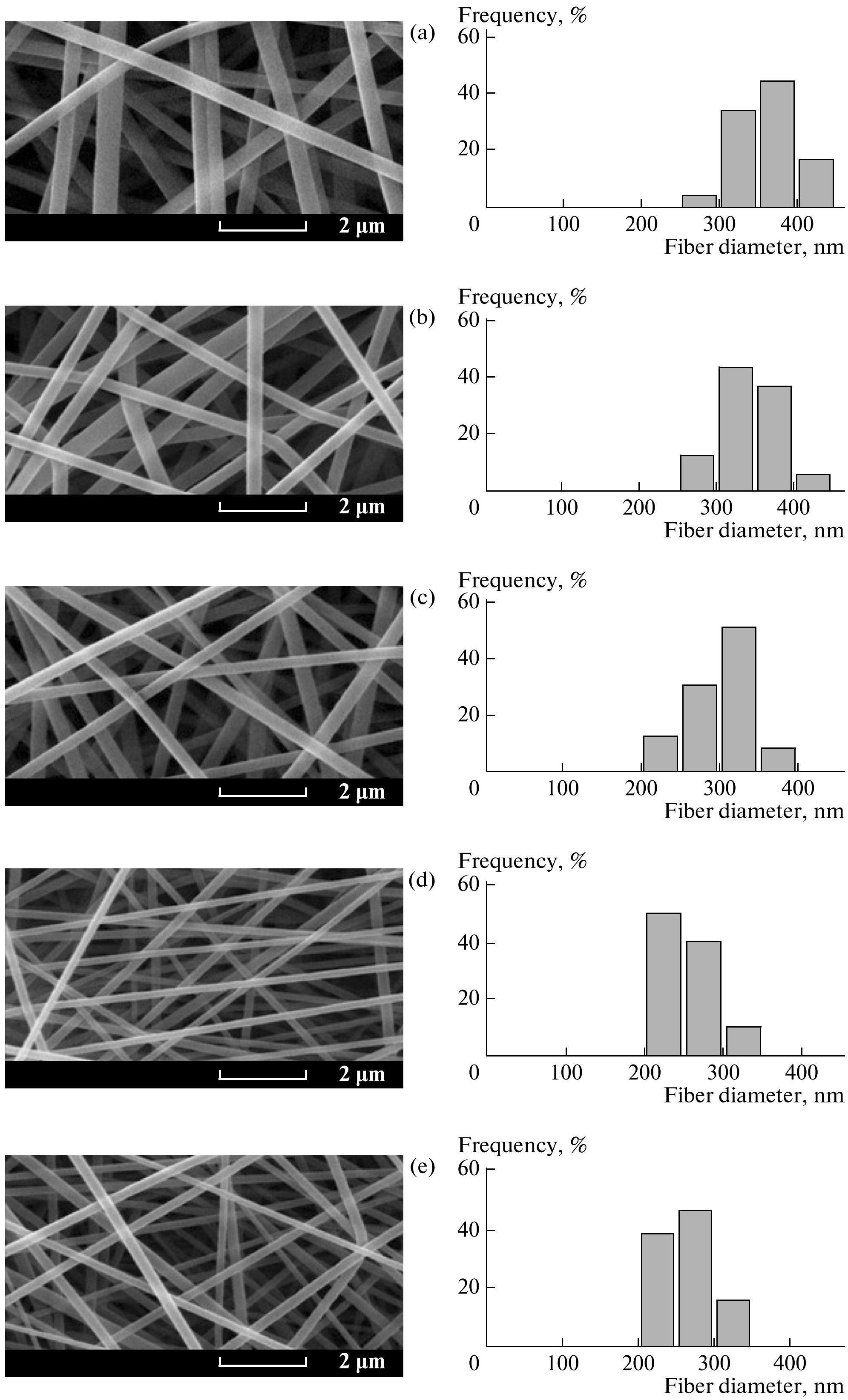

Fig. 6. Effect of spinning distance on morphology and fiber diameter distribution: (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25 cm (solution concentration: 13 wt %; applied voltage: 20 kV; $T = 30°C$; needle gauge number: 20).

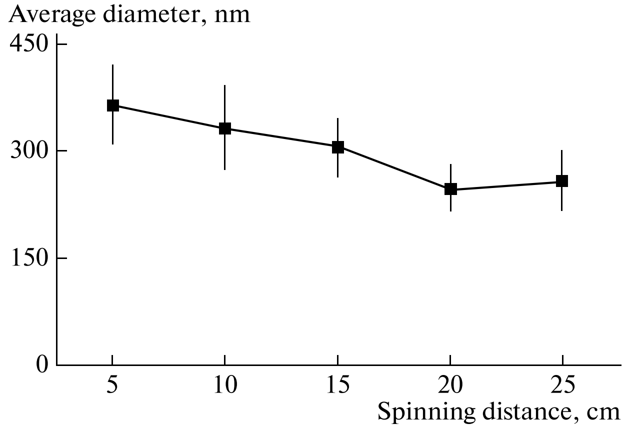

Fig. 7. The evolution of fiber diameter with increasing spinning distance (solution concentration: 13 wt %; applied voltage: 20 kV; $T = 30°C$; needle gauge number: 20).

average diameter of electrospun PAN fibers at various solution concentrations. It can be seen that the average fiber diameter noticeably increased as the solution concentration increased the larger diameter at high solution concentrations is probably due to extensive polymer chain entanglements, resulting in higher viscoelastic forces which tend to resist the electrostatic stretching force. These findings have good consistency with literature reports [19, 20].

Effect of Applied Voltage

Within the electrospinning process, there is a minimum applied voltage known as threshold voltage that is required to eject charged jet from Taylor cone. Threshold voltage depends mainly on the solution concentration. At higher concentrations, higher values of voltage are required to overcome both surface tension and the viscoelastic force for ejection of the jet. However, higher values than threshold voltage are needed to form continuous stable jets.

The effect of applied voltage on morphology and diameter of electrospun fibers is rather controversial. Generally, in case of applied voltage effects, there are two factors, i.e., strength of stretching solution and flight time of the jet. On the one hand, increasing the applied voltage, which is proportional to increasing the electric field strength, increases the electrostatic repulsive force on the fluid jet. This may cause greater stretching of the solution that finally leads to reduction in fiber diameter [18]. On the other hand, increasing the applied voltage may result in an increase in the acceleration of the jet, which decreases the flight time of the electrospinning jet. As a result, a lower flight time does not allow more time for the fibers to stretch and elongate before they are deposited on the collector, hence larger fiber formation. These two opposing factors may be the reason for contradicting literature reports on the effect of applied voltage. Previous studies have shown that increasing applied voltage may decrease [19, 20], may increase [17] or may not even change [21] the fiber diameter.

In this study, a series of experiments were carried out when the applied voltage was varied from 15 to 35 kV by 5 kV intervals using a 13 wt % solution. SEM micrographs and size distribution of PAN nanofibers of this study are shown in Fig. 4. It can be seen that bead-free fibers were fabricated in all 5 experiments, and the size distribution is almost constant in all nanofibers. Moreover, Figure 6 shows the influence of applied voltage on the average fiber diameter. Figure 5 depicts that by increasing applied voltage from 15 to 25 kV, fiber diameter decreased from 340 to 255 nm. This could be due to stronger electric field which causes greater stretching of the solution. However, as the applied voltage exceeds a limit (25kV), the flight time is low enough to be a determining factor. Hence, further increase in applied voltage results in an increase in fiber diameter. At higher applied voltages, the greater amount of the induced charges causes faster acceleration of the electrospinning jet and then more volume of polymer solution is drawn from the needle tip, which can explain the increase in fiber diameter in applied voltages higher than 25 kV.

Effect of Spinning Distance

As mentioned above, flight time and electric field strength affect the electrospinning process and the resultant fibers. The effect of spinning distance is almost the same as applied voltage. So, varying the distance between the tip and the collector has a direct influence on both the flight time and the electric field strength. The influence of the spinning distance on the morphology and diameter of the electrospun PAN nanofibers is evaluated using a solution with the constant concentration of 13 wt % at 20 kV. SEM micrographs and size distribution of resultant

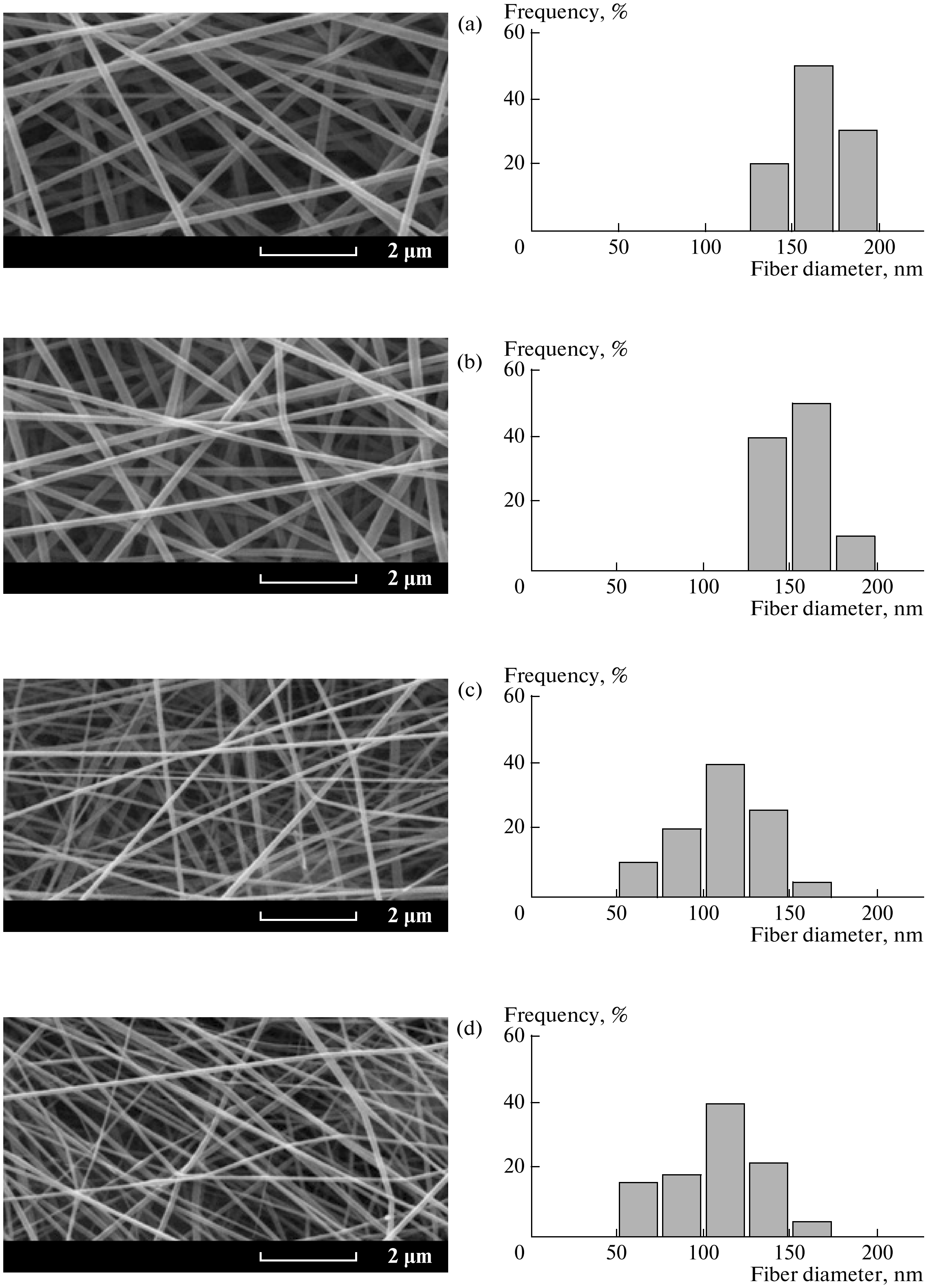

Fig. 8. SEM micrographs and diameter distribution of the PAN nanofibers obtained from surroundings temperature of (a) 20, (b) 25, (c) 30, and (d) 35°C (solution concentration: 10 wt %; applied voltage: 20 kV; spinning distance: 15 cm; needle gauge number: 20).

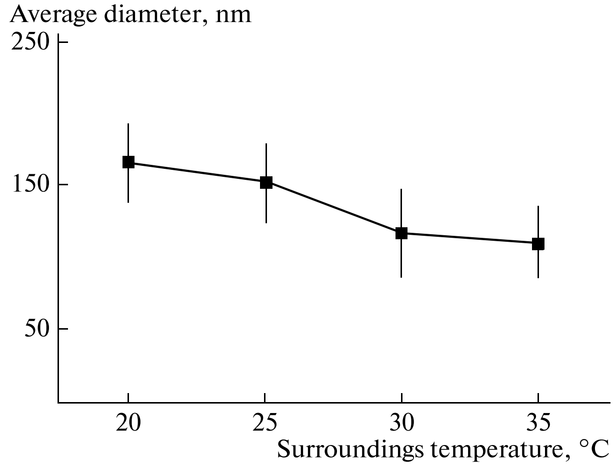

Fig. 9. Influence of surroundings temperature on average diameter of electrospun PAN nanofibers (solution concentration: 10 wt %; applied voltage: 20 kV; spinning distance: 15 cm; needle gauge number: 20).

nanofibers are shown in Fig. 6. From Fig. 6 it can be concluded that the solution concentration is high enough so as not to allow bead formation even at low spinning distances where the fibers may not have sufficient time to dry before reaching the collector. Also, size distribution is narrower when distance is above 20 cm. Moreover, Fig. 7 shows the influence of spinning distance on average nanofiber diameter. It can be seen that the graph is consisted of two parts. In the first part, increasing spinning distance from 10 to 20 cm brought about a continuous decrease in fiber diameter from 367 to 248 nm. The reason of this behavior could be higher flight time of the jet, despite lowering the electric field strength. However, in the second part, the diameter started to increase due to considerable decrease in electric field strength caused by larger distance.

Effect of Surroundings Temperature

Surroundings temperature can greatly affect both the volatilization of the solvent and the viscosity of the polymer solution. Not with standing these effects, there are a few studies investigating the influence of surroundings temperature as an electrospinning parameter [22].

In this study, in order to investigate the effect of surroundings temperature, a series of experiments were carried out when the temperature was varied from 20 to 35°C by 5°C intervals using a 10 wt % solution at applied voltage of 20 kV and spinning distance of 15 cm. SEM micrographs and size distribution of the resultant nanofibers are shown in Fig. 8. As it can be seen, bead-free nanofibers were prepared, and size distribution has been slightly widened in higher temperature. Furthermore, the influence of temperature on average diameter of electrospun PAN fibers is depicted in Fig. 9. As it can be seen, by increasing temperature from 20 to 30°C fiber diameter continuously decreases from 167 to 118 nm. However, at values higher than 30°C, the diameter did not change noticeably. Increasing temperature has the effects of reducing the viscosity of the polymer solution, increasing solvent evaporation rate, and also may cause greater solubility of the polymer in the solvent [18]. As a result of these effects, the coulombic forces would be able to exert a greater stretching force on the solution resulting in fabrication of thinner fibers.

Effect of Needle Diameter

To study the effect of needle diameter on the diameter and morphology of nanofibers, four different needles with 16, 17, 18, 19, 20 gauge numbers (1.19, 1.07, 0.84, 0.69, and 0.60 mm inner diameter, respectively) were used. Figure 10 shows SEM micrographs and size distribution of resultant nanofibers. It can be seen that bead-free fibers were fabricated in all experiments, and narrower size distribution was obtained using needle gage of 16. In addition, the effect of needle diameter on average fiber diameter is illustrated in Fig. 11. It is well-known that the surface tension of a droplet is increased with a decrease in its radius. When the size of the droplet at the tip of the needle is decreased, such as in case of a smaller internal diameter of the needle, the surface tension of the droplet increases. Therefore, for the same applied voltage, greater coulombic force is required to initiate electrospinning jet from Taylor cone. As a result, the acceleration of the jet decreases and the flight time for the solution becomes larger leading to more stretching of the solution. Thus, fibers with small diameter can be obtained by using a narrow needle, as shown in Figs. 10 and 11. However, the decrease in diameter was noticeable only between needle gauges of 18 and 19.

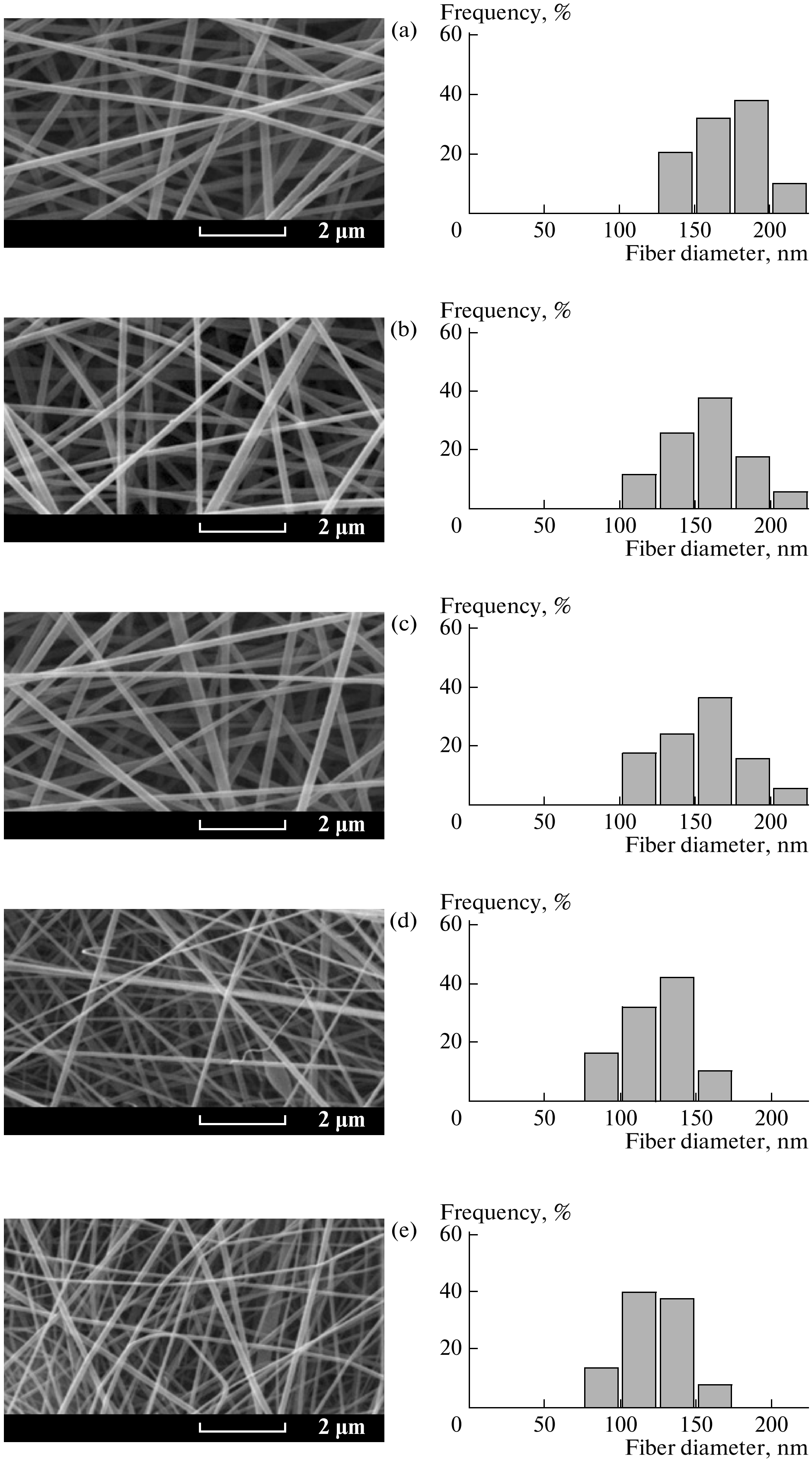

Fig. 10. SEM micrographs and diameter distribution of the PAN nanofibers at various needle diameters with (a) 16, (b) 17, (c) 18, (d) 19, (e) 20 gauge number (solution concentration: 10 wt %; applied voltage: 20 kV; spinning distance: 15 cm; $T = 30$°C).

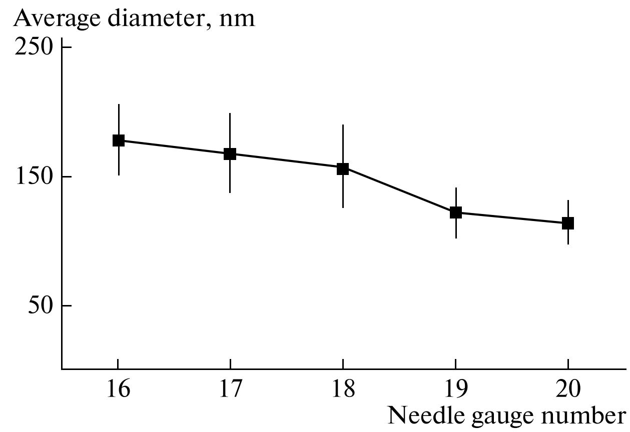

Fig. 11. Influence of needle diameter on average diameter of electrospun PAN nanofibers (solution concentration: 10 wt %; applied voltage: 20 kV; spinning distance: 15 cm; $T = 30°C$).

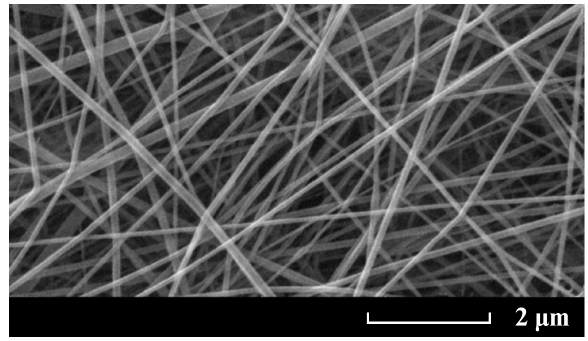

Fig. 12. SEM micrographs of nanofibers with minimum average diameter.

Preparation of Nanofibers with Minimum Diameter

In electrospinning process it is important to obtain nanofibers with minimum diameter, which provide maximum fiber surface area. According to the data obtained from the experimental study, the optimum conditions for fabricating bead-free nanofibers with minimum diameter were found to be solution concentration = 10 wt %, applied voltage = 25 kV, spinning distance = 20 cm, surroundings temperature = 35°C and needle gauge number = 20. Also, under these conditions, PAN nanofibers with diameter of 88 ± 14 nm were produced. The SEM micrograph for the prepared nanofibers is given in Fig. 12.

CONCLUSIONS

This study attempted to fabricate PAN nanofibers under different electrospinning conditions. The effects of electrospinning parameters such as solution concentration, applied voltage, spinning distance, surroundings temperature, and needle diameter on the morphology and diameter of the nanofibers were investigated. The results indicate that, as expected, the solution concentration has a significant effect on the morphology and diameter of the nanofibers. At the low solution concentration of 10 wt %, there were numerous beads on the fibers and the beads were disappeared above the solution concentration of 10 wt %. Also, by increasing the solution concentration from 7 to 19 wt % the nanofibers diameter increased from 84 nm to 757 nm. The behavior of nanofiber diameter as a function of applied voltage and spinning distance was almost the same. The increase in these two parameters had two opposing effects: at lower values of applied voltage and spinning distance, the diameter decreased gradually; and at higher values, a reversal was observed and diameter increased. Also, the nanofibers diameter slightly decreased with increasing and decreasing in the surroundings temperature and needle diameter, respectively. Under the optimal conditions, PAN nanofibers with minimum diameter of 88 nm were produced.

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