Determination of Optimal Production Parameters for Polyacrylonitrile Nanofibers

Ali Kirecci, Ümran Özkoç, H. İbrahim İçoğlu

Textile Engineering Department, University of Gaziantep, Gaziantep 27310, Turkey

Received 3 February 2011; accepted 6 September 2011
DOI 10.1002/app.35597
Published online 11 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The object of this work is to determine the most suitable values of process and solution parameters for electrospinning of polyacrylonitrile (PAN) nanofibers including solution concentration, applied voltage, and working distance between the needle tip and the collector plate. To investigate the effects of those parameters on the fiber morphology, nanofiber mat samples were produced by changing the value of parameters systematically. The scanning electron microscope images of these samples were analyzed to realize the effects of these parameters on the nanofiber morphology. Our results demonstrate that the diameter of the fibers increases with increasing concentration. However, the diameter reduces as the applied voltage and working distance between needle tip and the collector increase up to a certain value. In addition to this, viscosity and applied voltage have a strong effect on the uniformity and morphology of the nanofibers. Moreover, a relationship between spinning distance, voltage supplied, solution concentration, charge density, bead formation, and the diameter of the electrospun PAN nanofiber were established in the study. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4961–4968, 2012

Key words: electrospinning; polyacrylonitrile; optimization; concentration; nanofiber

INTRODUCTION

Electrospinning is the most effective method to produce superfine fibers ranging from some hundred nanometers up to 1 μm.[1,2] The process is simple and lower cost than any other processes that can produce nanoscale fibers. The electrospinning process involves the application of a strong electrostatic field to a capillary connected with a reservoir containing a polymer solution. The high applied voltage will induce electric charge to the solution and once electrostatic force overcomes the surface tension of solution, viscoelastic force nanofibers are produced.[3–5]

The morphology of electrospun nanofibres are dependent on the solution parameters (polymer molecular weight, viscosity, conductivity, volatility of solvent, and surface tension), the processing parameters (applied voltage, feed rate, type of collector, diameter of nozzle, and tip–collector distance) and the ambient parameters (humidity, temperature, and type of atmosphere).[6–8] The solution must have a surface tension low enough, a charge density high enough, and a viscosity high enough to prevent the jet from collapsing into droplets before the solvent has evaporated.[9–14]

Solution concentration has a significant effect on the final size and distribution of particles. Varying solution concentration alters the morphology of the nanofibers formed. At the low concentrations, the fibers have beads, which are irregular, undulating morphology with large variations in diameter along a single fiber. At high concentrations, the nanofibers have a regular, cylindrical morphology, and have a larger and more uniform diameter.[15–18] Higher environment temperature has a tendency to increase the fiber diameter and better diameter uniformity of the fibers.[19]

The applied voltage has an influence in the stretching and on the morphology of the fibers obtained. In most cases, a higher voltage will lead to greater stretching of the solution due to the greater columbic forces in the jet as well as the stronger electric field. These have the effect of reducing the diameter of the fibers and also encourage faster solvent evaporation to yield drier fibers.[20,21] The number of deposited fibers also increases with the applied voltage.[22] Another important parameter for the electrospinning process is the conductivity of the solution that may have a great effect on fiber diameter.[23] Some amount of salt may be added to polymer solution to reduce the fiber diameter.[24]

Depending on the solution property, the effect of varying the distance may have a significant effect on the fiber morphology. The formation of beads may be the result of increased field strength between the needle tip and the collector. Decreasing the distance has the same effect as increasing the applied voltage

Correspondence to: A. Kirecci (kirecci@gantep.edu.tr).
Contract grant sponsor: University of Gaziantep BAPYB; contract grant number: MF.08.04.

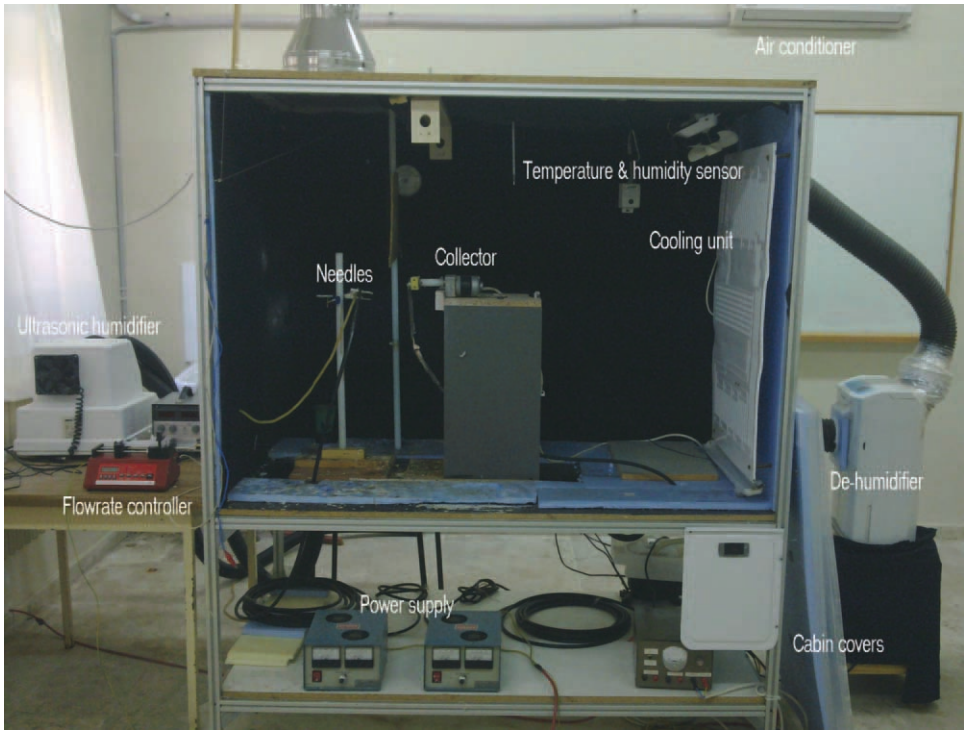

Figure 1 Electrospinning set up. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

supplied and this will cause an increased in the field strength. If the field strength is too high, the increased instability of the jet may encourage beads formation.[5,13,20]

During the last 10 years, extensive researches have been conducted on various aspects of electrospinning. Polyacrylonitrile (PAN) is one of the most extensively used polymers in many areas such as in filtration, biomedical application, protective clothing, tissue engineering, and composite fabrics and materials because of its excellent properties.[25–28] The nanofiber mats containing finer nanofibers show higher specific surface area and higher porosity. These properties make nanofibers attractive for tissue engineering scaffolds, drug delivery systems, catalyst and enszyme supports, sensors, and other applications in biology, medicine, and controlled release.[29]

The study aims to determine the optimal values of basic parameters to produce the finest and uniform nanofibers without beads for electrospinning of PAN nanofibers. In the study, the ranges of parameters (applied voltage, tip–collector distance, and concentration) were selected wider than previous studies. These wider ranges provide some additional results to the available literature. The experimental results show that the nanofiber diameter reduces as the applied voltage increases as usual. However, the study, in addition to the literature, shows also that the fiber diameter increases after a certain value of applied voltage. Similar results were also obtained for the relationship between nanofiber diameter and needle tip–collector distance.

MATERIALS AND METHODS

Electrospinning system

PAN nanofibers were electrospun using an apparatus composed of two adjustable DC high voltage sources (−50 kV and +50 kV), a multiple spinneret system and a movable collector. The apparatus were established in a closed cabin to control temperature and humidity values. Positive high voltage source was used to charge the nozzles, whereas the negative voltage was used to charge the collector. The cabin has a cooling and a heating system to set the required temperature. The walls of the cabin were coated with an insulating material to reduce heat transfer during the process. Similarly, a humidifier

TABLE I
Solution Properties

Concentration (wt %)	Conductivity (mS/cm)	Viscosity (mPas)	Surface tension (mN/m)
6	84.7	478.5	37.24
8	82.6	588.5	38.07
10	76.5	698.5	38.92
12	67.5	808.5	39.32
14	56.8	918.5	39.99
16	46.2	1030.5	40.43

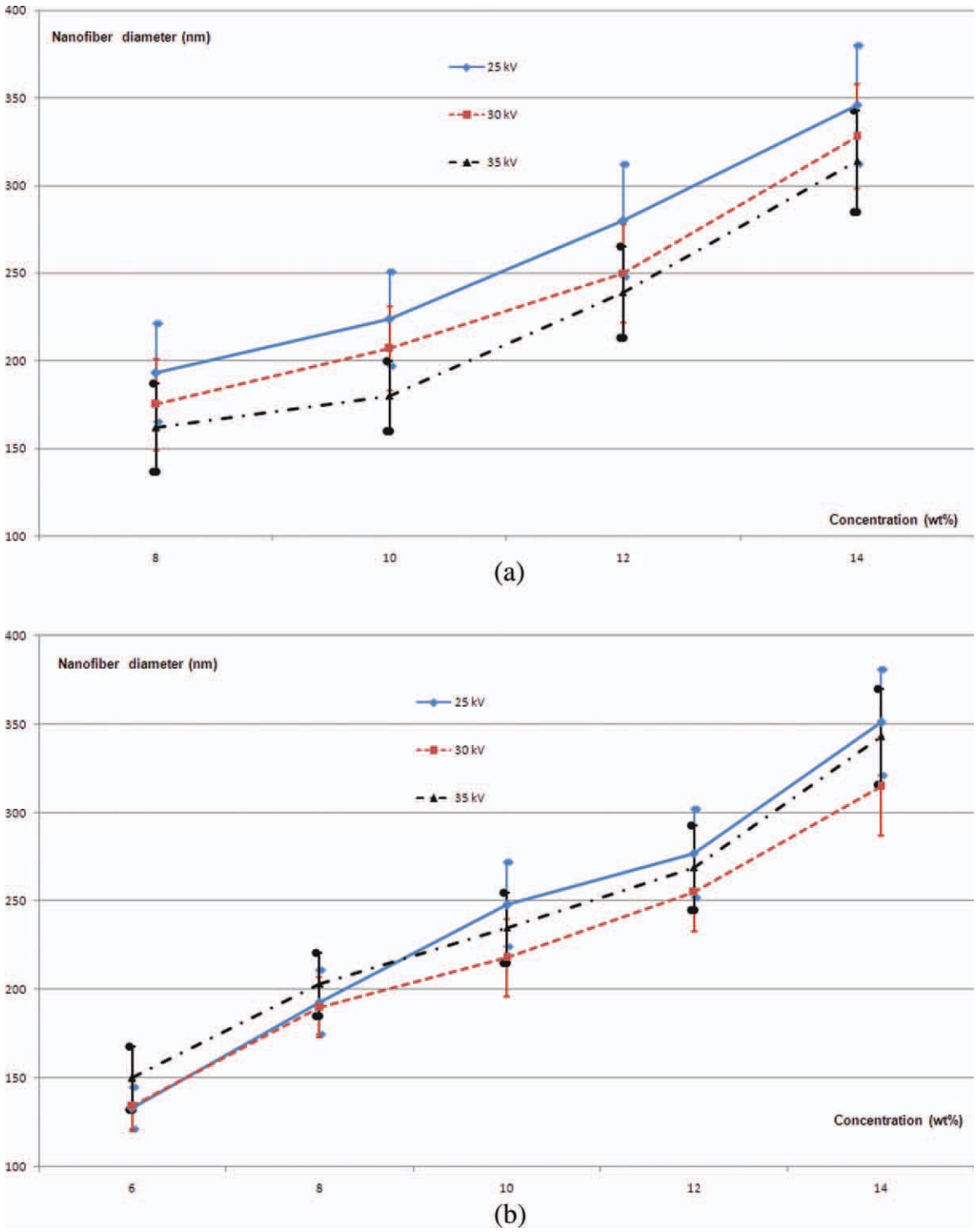

Figure 2 Effect of concentration on PAN nanofiber diameter. (a) Tip–collector distance 10 cm; (b) tip–collector distance 15 cm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was used to control the humidity value inside the cabin. An adjusting mechanism was used to set the desired distance between the nozzles and the collector. The collector was a brass rectangular plate which was jointed to motor shaft eccentrically to obtain uniform nanofiber distribution while the motor rotates. Also, a chimney was used to discharge the solvent vapor and freely flying nanofibers from the cabin. The experimental setup is given in Figure 1.

Nanofibers were collected on the aluminum foil in the form of nanofiber mats. The flow rate and jet diameters were selected as 0.5 mL/hour and 0.7 mm, respectively. Three nozzles (with 3 cm interval

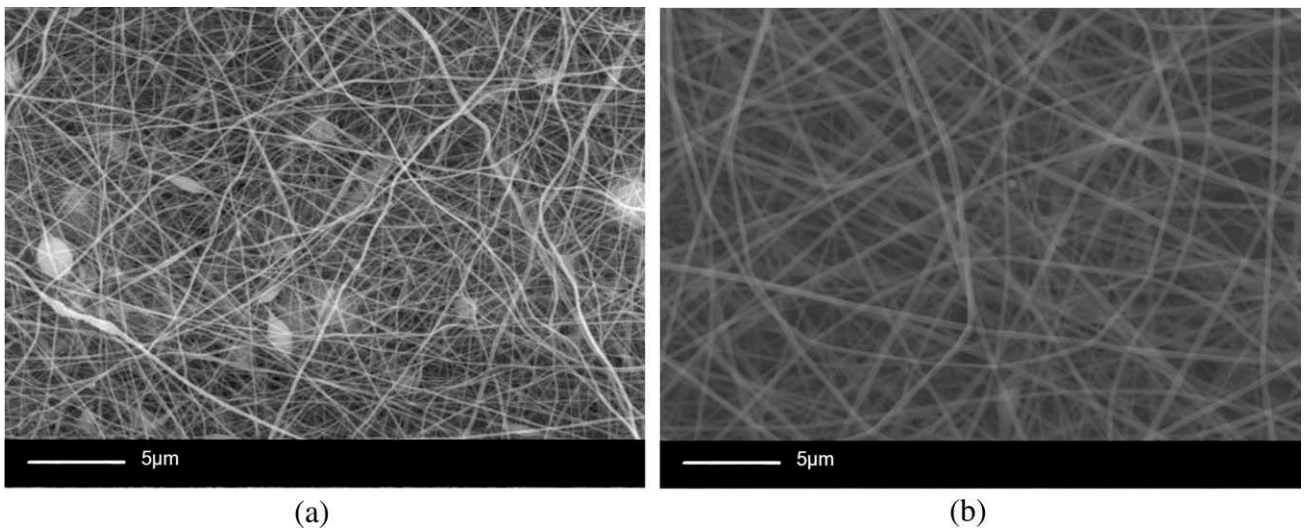

Figure 3 Effect of concentration on PAN nanofiber diameter (10 cm and 25 kV). (a) Concentration 6 wt %; (b) concentration 10 wt %.

in horizontal position) were used. During the experimental study the ambient parameters were kept constant (temperature 20°C and humidity 50%). The other parameters such as concentration, applied voltage, and tip–collector distance were discussed in further sections.

The morphological appearances of PAN nanofiber mats were investigated by a JEOL JSM-6390LV scanning electron microscope (SEM). Image-Pro Plus 6.0 program was used for measurement of diameters of nanofibers. Diameters of nanofibers were calculated by taking the average of 50 measurements.

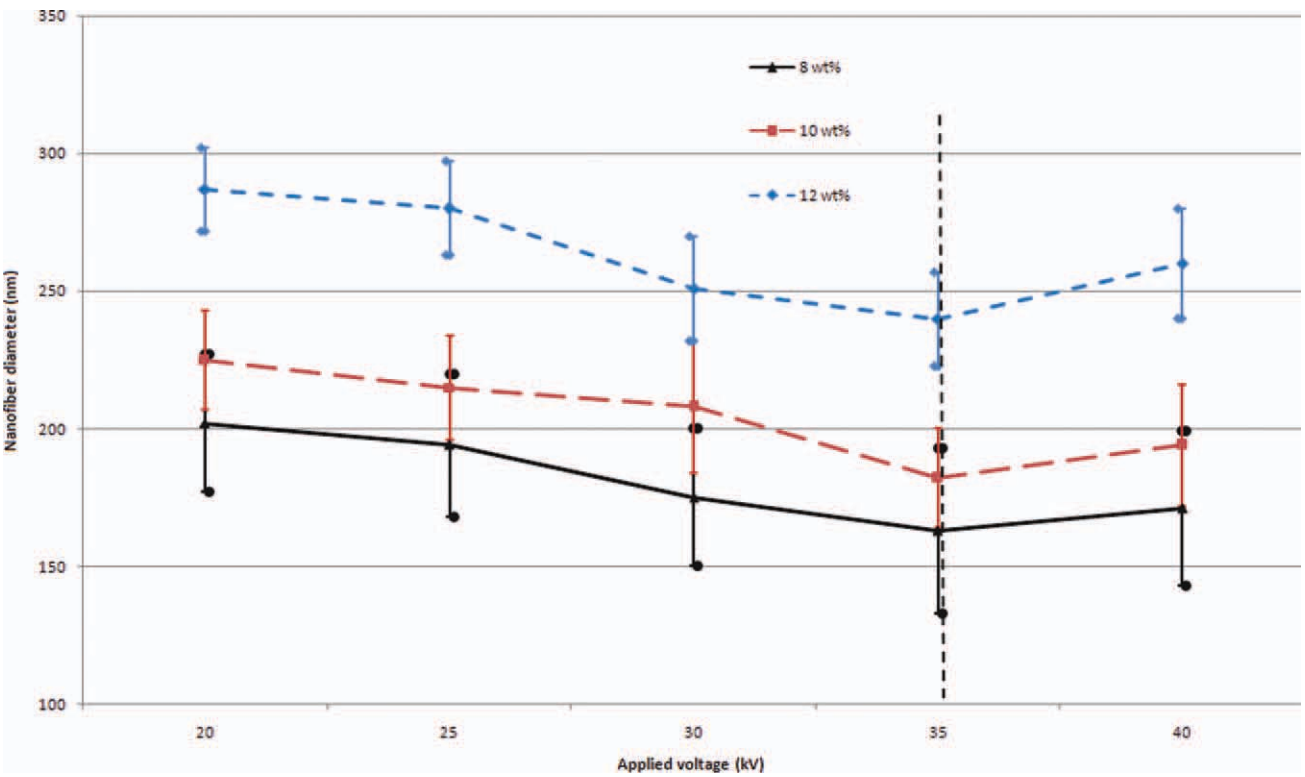

Figure 4 Effect of voltage on PAN nanofiber diameter (needle tip–collector distance is 15 cm).[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

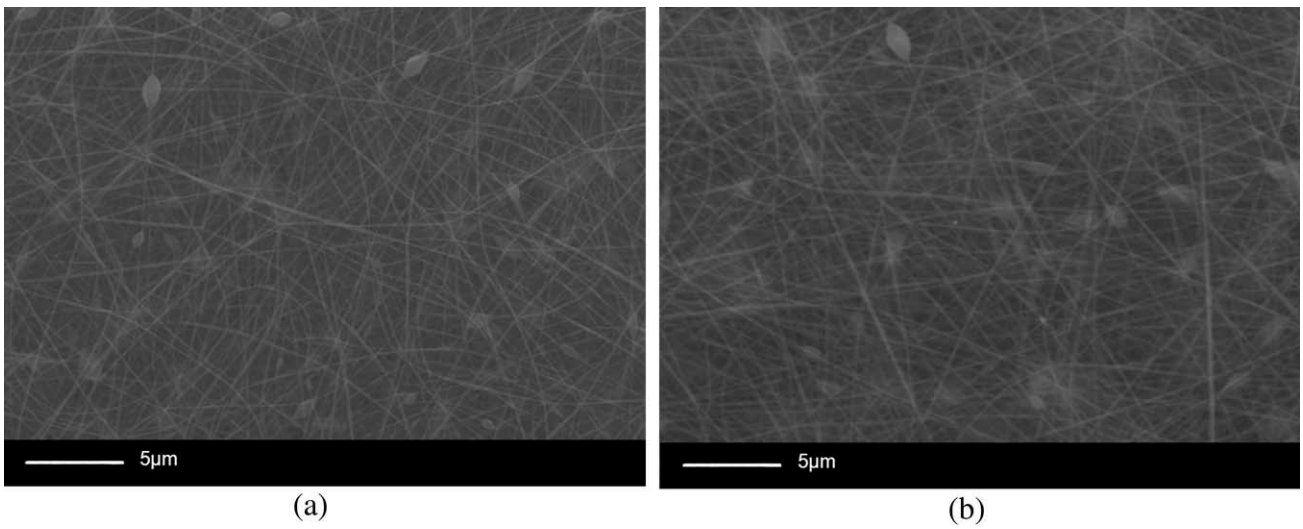

Figure 5 Effect of voltage on PAN nanofiber diameter (8 wt % and 15 cm). (a) Voltage 25 kV; (b) voltage 40 kV.

Materials and preparation of spinning solutions

PAN polymer (M_w 150,000) was gently supplied from AKSA Acrylic. The solutions were prepared by dissolving PAN polymer in dimethylformamide (DMF) by stirring magnetically for 3 hours at a temperature of 90°C. Viscosity, conductivity, and surface tension of the solutions were determined by Brookfield DV-III viscometer, Orion 4 star conductivity meter, and KSV CAM 101 surface tension meter, respectively.

RESULTS AND DISCUSSION

Apparently, to obtain uniform ejection of the charged jet, the spinning solution with a proper concentration is required. Generally, lower concentrations generate

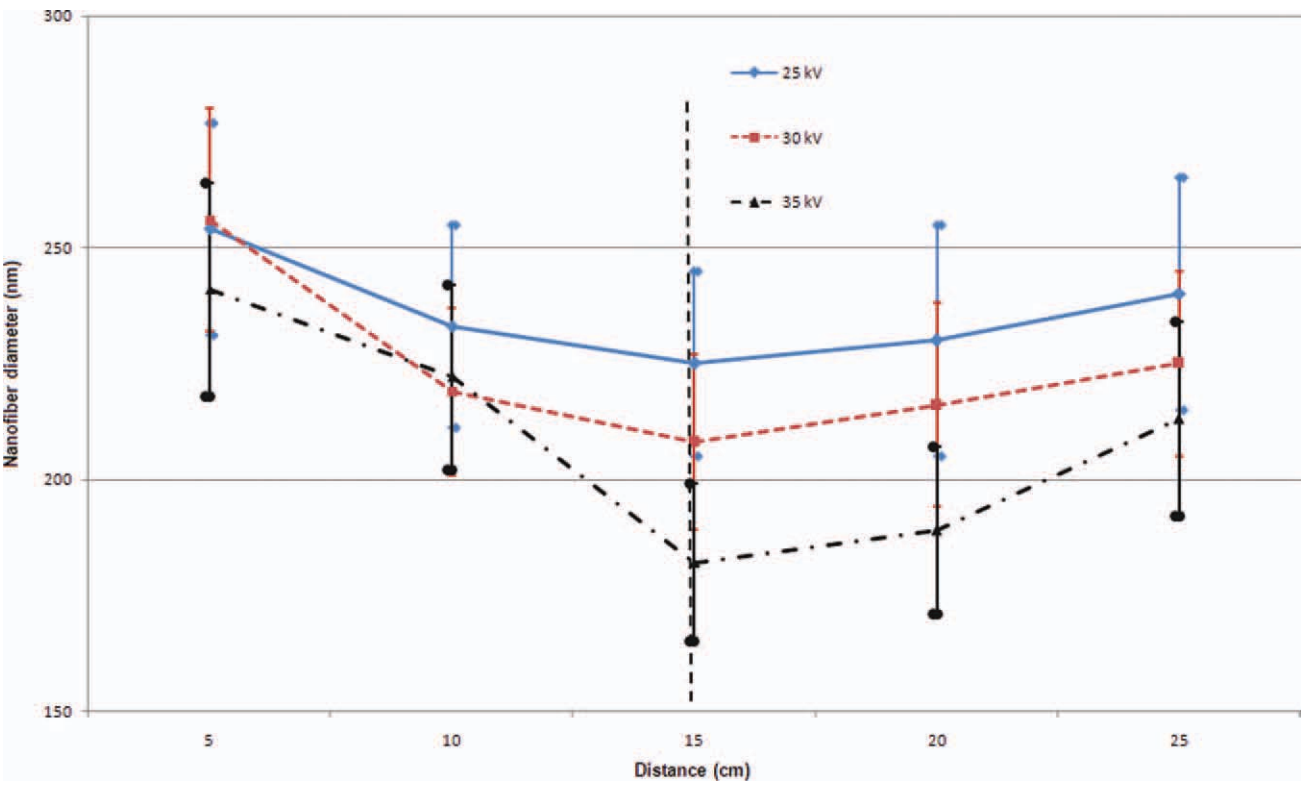

Figure 6 Effect of needle tip–collector distance on PAN nanofiber diameter (10 wt %).[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

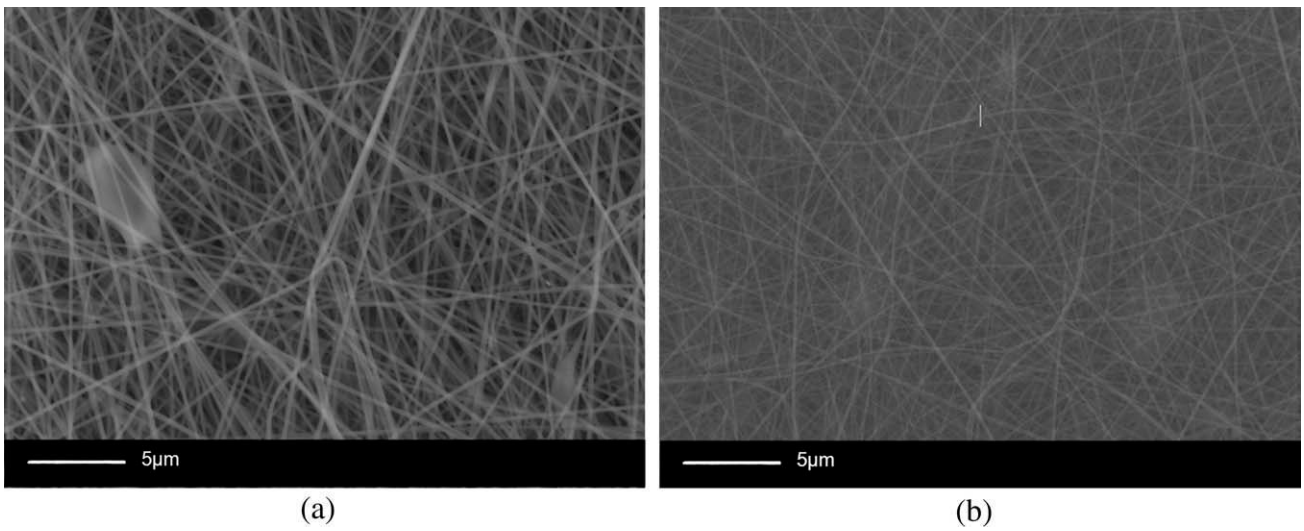

Figure 7 Effect of distance on PAN nanofiber diameter (30 kV and 10 wt %). (a) Tip–collector distance 5 cm; (b) tip–collector distance 15 cm.

beads and higher concentrations produce larger nanofiber diameter. Therefore, the solution concentration should be prepared properly so that the electrospinning process generates fine nanofibers without beads. PAN solutions were prepared from 6 to 16 wt % by 2 wt % intervals to investigate the effect of concentration on the nanofiber morphology. Table I shows the solution properties.

Solution properties such as surface tension, viscosity, and conductivity are effective on determining the amount of stretching of the solution in electrospinning process. Surface tension is effective on bead formation. At lower viscosity, there is a higher potential of occurrence of beaded fibers. If conductivity of the solution is higher, more charges can be carried in electrospinning.[9] Table I shows that the PAN solutions with low concentrations have higher conductivity, lower viscosity, and lower surface tension. This situation causes to decreasing of viscoelastic force while increasing the electrostatic force in electrospinning process. Therefore, the finer nanofibers with beads were obtained at low concentration values as expected (Fig. 2).

These solutions were converted into nanofiber mats by electrospinning at different voltage values and tip–collector distances. The effect of concentration on PAN nanofiber diameter is given in Figure 2(a,b). The experimental results show that the nanofiber diameter increases as the concentration increases at different voltage values and at different tip–collector distances. At low concentrations (less than 8 wt %) the electrospinning process generates a mixture of fibers and beads as shown in Figure 3(a). When concentration value was 8 wt %, bead formations were still observed in some cases, especially, at short tip–collector distance and at higher voltage values. However, bead formations were diminished almost completely after increasing the concentration to 10 wt % [Fig. 3(b)].

To examine the effect of voltage on nanofiber diameter, nanofiber mats were produced by increasing the applied voltage from 5 to 40 kV (5 kV intervals) regularly. The resultant relationship between the nanofiber diameter and the applied voltage is given in Figure 4. This figure shows that the fiber diameter decreases steadily up to 35 kV then the diameter of the nanofibers demonstrates a tendency of increasing the diameter interestingly which was not observed in the previous studies. The reason of this may be explain as the diameter of nanofibers reduces as applied voltage increases as shown in the first part of the graph (see left side of dashed line in Fig. 4) due to the increasing of electrostatic field and repulsion forces as stated in the previous studies.[18,22]

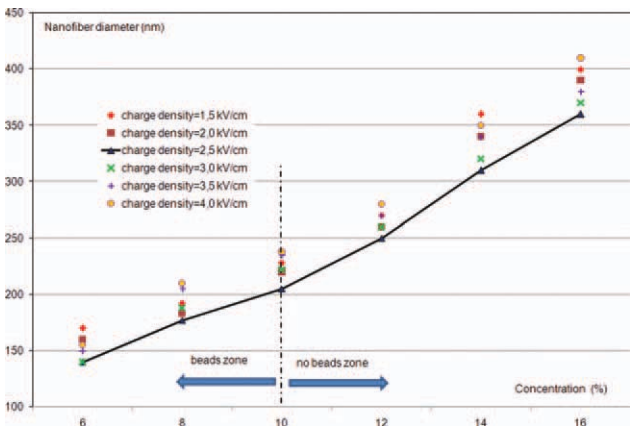

Figure 8 Charge density curves.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
The Average PAN Nanofiber Diameter According to Concentration and Charge Density

Concentration (wt %)	Charge density (kV/cm)					
	1.5 (nm)	2 (nm)	2.5 (nm)	3 (nm)	3.5 (nm)	4 (nm)
6	170 ± 20	160 ± 23	140 ± 20	143 ± 18	150 ± 17	155 ± 25
8	192 ± 28	183 ± 19	177 ± 25	188 ± 28	205 ± 26	210 ± 30
10	228 ± 31	220 ± 31	205 ± 24	222 ± 27	235 ± 22	238 ± 33
12	270 ± 25	260 ± 27	250 ± 32	260 ± 22	270 ± 35	280 ± 34
14	360 ± 36	340 ± 34	310 ± 30	320 ± 34	340 ± 33	350 ± 40
16	400 ± 44	390 ± 43	360 ± 36	370 ± 40	380 ± 37	410 ± 46

However, further increasing of applied voltage reduces the flight time (electrospinning time) of nanofibers. Lowering the flight time too much influences the stretching process and stretching time adversely. As a result of this, the diameter increases as shown in the second part of the graph (see right side of the dashed line in Fig. 4). The ranges of applied voltages, in previous studies, were selected usually as less than 35 kV. Therefore, they were obtained as a result of continuous decreasing of nanofibers in their studies, which may correspond to just the first part of Figure 4.[18,22]

Another consequence of the study is that the higher applied voltage increases the number of beads in the nanofiber mats as given in Figure 5(a,b). The effect of the needle tip and collector distance was examined by changing the distance from 5 to 25 cm with 5 cm intervals. The relationship between the nanofiber diameter and tip–collector distance is given in Figure 6. The experimental results show that the nanofiber diameter decreases as the distance increases approximately up to 15 cm then the diameter increases for larger distances gradually. The reason may be explained as follows: the diameter of nanofibers continuously decreases in the first part of the graph (see left side of dashed line in Fig. 6) due to longer flight time (distance) despite lowering the electrostatic force as mentioned in previous studies.[18,19,21,22] However, in the second part of the graph (see right side of dashed line in Fig. 6), the diameter starts to increase due to lowering of too much of electrostatic force caused by larger needle tip and collector distance. Thus, too low electrostatic force leads to larger nanofibers even at longer flight times.

Moreover, the experiments show that lowering the distance causes bead formation (due to less time for evaporation of solvent) and spark formation between the needle tip and the collector [Fig. 7(a)]. However, the productivity reduces considerably at longer distances (20 or 25 cm).[22] Consequently, the most effective results were obtained at 15 cm distance [Fig. 7(b)].

Determination of the optimal values of parameters

The data obtained from the experimental study is converted to a graph which gives a relationship between solution concentration and nanofiber diameter at different charge densities as given in Figure 8. The figure also gives an understanding about which conditions cause bead formation. The minimum limit for solution concentration to produce nanofibers without beads is determined as 10 wt % including the charge densities from 1.5 to 4.0 kV/cm as shown in Figure 8. The graph consists of six curves but one of them was drawn as a continuous curve that was determined as the most proper charge density curve (2.5 kV/cm), because it provides the most quality nanofiber (finest diameter) in the "no bead formation" zone. Table II shows the diameter results of the nanofibers according to the charge density and concentration.

To produce the desired nanofiber, users may determine the concentration depending on the nanofiber diameter by using the solid curve in the graph as the first step. The second step is to decide distance or applied voltage. Since, there are many

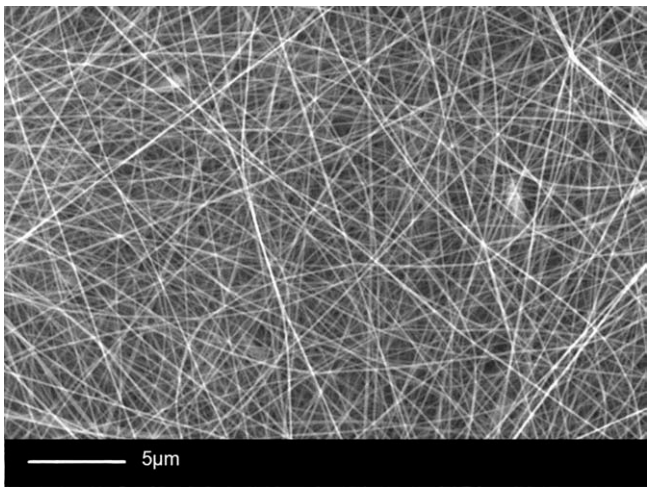

Figure 9 The SEM image of PAN nanofiber sample produced under the optimal conditions (10 wt %, 35 kV and 15 cm).

possibilities for those parameters to give the same result. Therefore, one of them should be selected to calculate the other by means of the charge density. Alternatively, the optimal values may be determined directly by selecting minimum solution concentration (10 wt %) because it provides minimum nanofiber diameter without beads. The applied voltage and tip–collector distance values can be selected as 35 kV and 15 cm, respectively. Those values were determined as the optimal values in the previous sections. The SEM image of the nanofiber sample produced under the optimal conditions is given in Figure 9.

CONCLUSION

This study shows a procedure to determine optimal values of basic electrospin parameters of PAN nanofibers. During the study, it was observed that the solution concentration is the most dominant parameter to affect the nanofiber diameter (as already declared by many researchers). Lower solution concentration produces finer nanofiber diameters but at the same time supports bead formation. On the other side, raising the concentration increases the diameter. Experimentally, the most appropriate concentration value was determined as 10 wt %, which applicable for charge densities from 1.5 to 4.0 kV/cm. The ranges of applied voltage and needle tip–collector distance were selected wider than previous studies. Consequently, it was observed that the voltage versus nanofiber diameter and the distance versus nanofiber diameter curves have inflection points. The diameter of nanofiber initially decreases dawn to the inflection point than increases in both curves (Figs. 4 and 6). Therefore, these inflection points were accepted as optimal values for needle tip–collector distance and applied voltage. Thus, the finest fibers without bead formation can be obtained by 10 wt % solution concentration at 15 cm needle tip–collector distance by applying 35 kV voltage difference. Those values were obtained with three spinnerets in a horizontal line at 0.5 mL/hour flow rate, 20°C temperature, and 50% relative humidity.

The experimental results show that there are different possibilities that may satisfy the required thickness of nanofiber. Therefore, a charge density graph was prepared to determine the values of parameters (applied voltage and tip–collector distance) to obtain desired nanofiber diameter without bead formation. The solution concentration may be obtained according to the desired nanofiber diameter using this graph. Then applied voltage and distance values can be determined by selecting one of these parameters.

The authors acknowledge to Gaziantep University.

References

1. Formhals, A. US Pat. 1 975 504, 1934.
2. Kowalewski, T. A.; Blonski, S.; Barral, S. Bul Polish Academy Sci Tech Sci 2005, 53, 385.
3. Doshi, J.; Reneker, D. H. J Electrostat 1995, 35, 151.
4. Reneker, D. H.; Chun I. Nanotechnology 1996, 7, 216.
5. Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. J Appl Phys 2000, 87, 453.
6. Zong, X.; Kim, K.; Fang, D.; Ran, S.; Hsiao, B. S.; Chu, B. Polymer 2002, 43, 4403.
7. Saiyasombat, C.; Maensiria, S. J Polym Eng 2007, 27, 8.
8. Jalili, R.; Morshed, M. J Appl Polym Sci 2006, 101, 4350.
9. Ramakrishna, S.; Fujihara, K.; Teo, W. E.; Yong, T.; Ma, Z. Mater Today 2006, 9, 40.
10. Fennessey, S. F.; Farris, R. J. Polymer 2004, 45, 4217.
11. Lin, T.; Wang, H. X.; Wang, H. M.; Wang, X. G. J Mater Sci Tech 2005, 21, 9.
12. Samatham, R.; Kim, K. J. Polym Eng Sci 2006, 46, 954.
13. Megelski, S.; Stephens, J. S.; Chase, D. B.; Rabolt, J. F. Macromolecules 2002, 35, 8456.
14. Bognitzki, M.; Czado, W.; Frese, T.; Schaper, A.; Hellwig, M.; Steinhart, M.; Greiner, A.; Wendorff, J. H. Adv Mater 2001, 13, 70.
15. Deitzel, J. M.; Kleinmeyer, J.; Harris, D.; Tan, N. C. B. Polymer 2001, 42, 261.
16. Lingaiah, S.; Shivakumar, K. N.; Sadler, R.; Sharpe, M. I. SAMPE Symposium and Exhibition, Baltimore, MD 2007, 52, 11.
17. He, J. H.; Wan Y. Q.; Yu, J. Y. Fib Polym 2008, 9, 140.
18. Wang, T.; Kumar, S. J Appl Polym Sci 2006, 102, 1023.
19. El-Fattah, A. Carbon nano tube reinforced carbon nano composite fibrils by electro-spinning, Ph.D. Thesis, Materials Engineering, Drexel University, Philadelphia, 2002.
20. Fujihara K.; Ramakrishna S. An introduction to electrospinning and nanofibers, National University of Singapore, 2005.
21. Jalili, R.; Hosseini S. A.; Morshed M. Iran Polym J 2005, 14, 1074.
22. Gomes, D. S.; Silva, A. N.; Morimoto, N. I. Polimeros 2007, 17, 206.
23. Heikkila, P.; Harlin, A. Express Polym Lett 2009, 3, 437.
24. Qina, X.; Wana, Y. Polymer 2004, 45, 6409.
25. Huang, Z. M.; Zhang, Y. Z.; Kotakic, M.; Ramakrishna, S. Compos Sci Tech 2003, 63, 2223.
26. Gibson, P. W.; Lee, C.; Ko, F.; Reneker, D. J Eng Fiber Fabric 2001, 2, 32.
27. Sawhney, A. P.; Condon, B.; Singh, K. V.; Pang, S.S.; Li, G.; Hui, D. Text Res J 2008, 78, 731.
28. Qian, L.; Hinestroza, J. P. Tech Manag 2004, 4, 1.
29. Rutledge, G. C.; Fridrikh S. V. Adv Drug Deliv Rev 2007, 59, 1384.