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The Effects of Operating Parameters on the Morphology of Electrospun Polyacrilonitrile Nanofibres

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ABSTRACT

Polyacrilonitrile (PAN) nanofibres were prepared by electrospinning of PAN/DMF solution of 15 % wt concentration. Fibre morphology was observed under a scanning electron microscopy. The effects of operating parameters including applied voltage, feeding rate and tip-target distance on the morphology of electrospun PAN nanofibres were systematically evaluated. Average diameters of nanofibres decreased with increasing applied voltage from 10 to 20 kV, but broader distribution in diameters of nanofibres were obtained at 15 kV and above. Morphology of nanofibres was changed by the instability of the liquid surface from which the jet originates to beaded nanofibres. The morphological structure can be changed by changing the feeding rate of solution and tip-target distance. At lower and higher feeding rates, nanofibres with beades were observed. At 7.5 cm tip-target distance and below, the structures of nanofibres appeared not to be stabilized completely, indicating that the spun nanofibres were mostly wet when they reached the collecting target.

Key Words:
polyacrilonitrile;
nanofibers;
morphology;
operating parameters

INTRODUCTION

Fibres of synthetic polymers have been produced for decades by conventional processes, such as melt spinning, dry spinning, and wet spinning. These techniques rely upon pressure-driven extrusion of a viscous polymer fluid and produce fibres that typically range from 10 to 500 μm diameter [1]. Electrospinning is a novel process for forming fibres with nano-scale diameters through the action of electrostatic forces. In a typical process an electrical potential is applied between

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droplet of polymer solution, or melt, held through a syringe needle and a grounded target. Electrostatic charging of the droplet results in the formation of the well-known Taylor cone. When the electric forces overcome the surface tension of the droplet from the apex of the cone, a charged fluid jet is ejected [2]. The jet exhibits bending instabilities due to repulsive forces between the surface charges, which is carried with the jet, and follows a looping and spiraling path [3, 4] (Figure 1). The electrical forces elongate the jet thousands of times and the jet becomes so thin. Ultimately, the solvent evaporates, or the melt solidifies and very long nanofibres are collected on the grounded target [2].

The morphology and diameter of electrospun nanofibres are dependent on a number of processing parameters that include.

(a) the intrinsic properties of the solution such as the type of polymer and solvent, polymer molecular weight, viscosity (or concentration), elasticity, conductivity, and surface tension [5-10].

(b) the operational conditions such as the applied voltage, the distance between spinneret and collector (tip-target distance), and the feeding rate of the polymer solution [8, 11, 12].

In addition to these variables, the humidity and temperature of the surroundings may also play an important role in determining the morphology and diameter of electrospun nanofibres [13]. For instance, the polymer solution must have a concentration high enough to cause polymer entanglements yet not so high that the viscosity prevents polymer motion induced by the electric field. The solution must also 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 [14].

Son et al. showed that, the average diameter of poly(ethylene oxide) (PEO) nanofibres decrease with increasing PEO solution conductivity and solvent polarity [7]. Son et al. reported that, the average diameter of cellulose acetate (CA) nanofibres was not significantly changed by changing operating parameters, but increases by increasing CA solution concentration [8].

Zhang et al. found that, with increasing applied voltage the average diameter of the poly(vinyl alcohol) (PVA) nanofibre increases slightly but the distribution of diameter of fibres is increased, and tip-target distance did not have significant effects on fibre morphology [11]. Wannatong et al. reported that, in electrospinning of polystyrene (PS) solutions, at first the fibre diameters slightly decrease with increasing applied voltage, and then increase with further increase in the applied voltage [9].

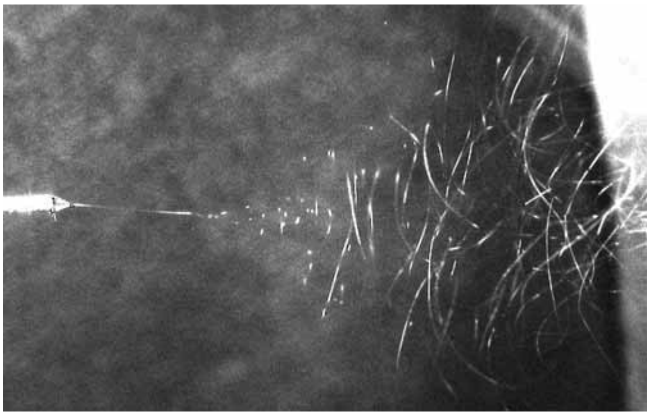


Figure 1. Image of electrospinning of 15 % wt PAN/DMF solution. The single jet goes through bending instability.

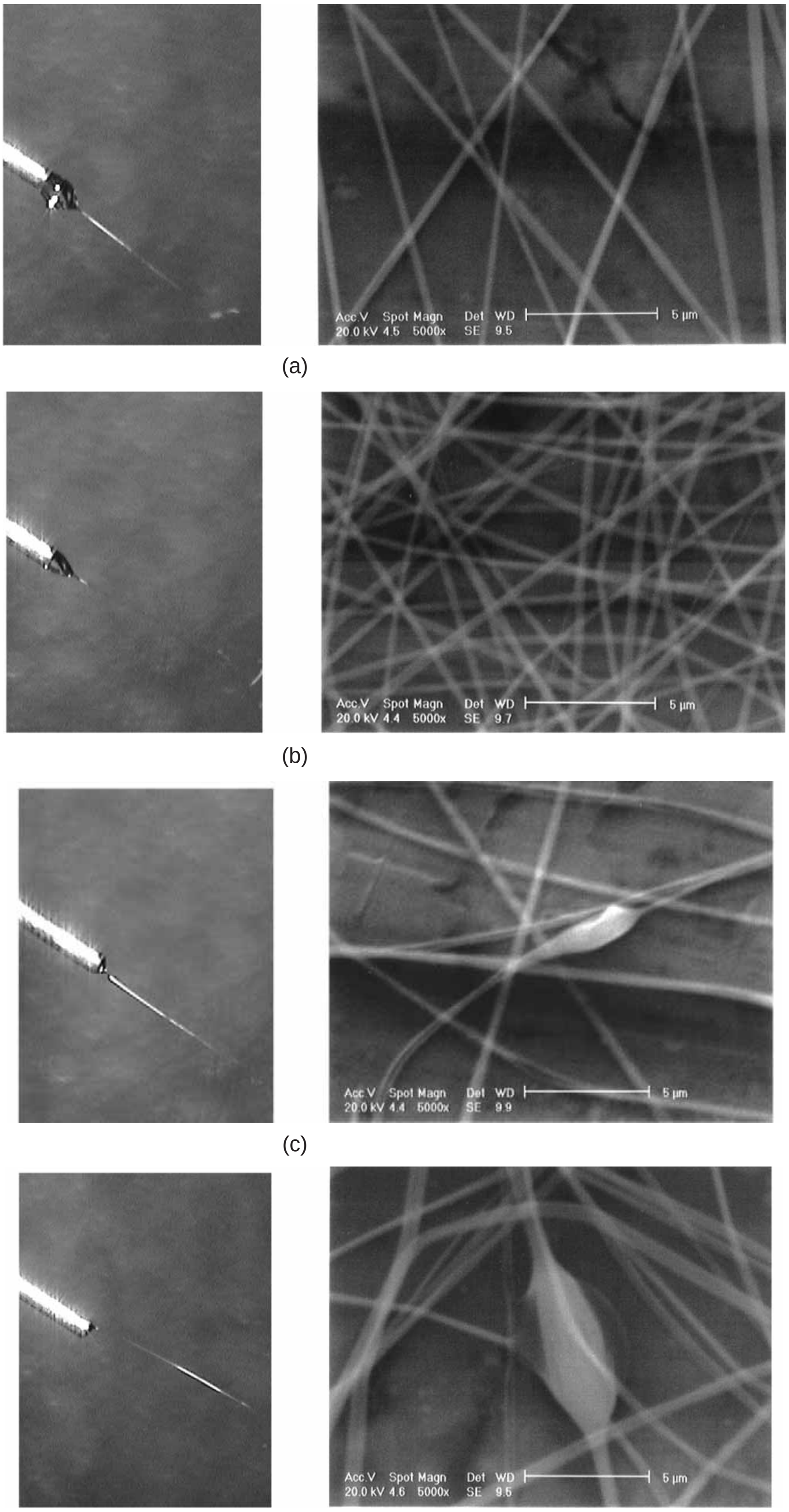
Deitzel et al. found that the morphology of the PEO nanofibres is influenced strongly by parameters such as feeding rate of the polymer solution and the electrospinning voltage. At constant feeding rate, by increasing the voltage of Electrospinning, the shape of the surface is changing from what the electrospinning jet originates. Therefore, there was a decrease in the stability of the initiating jet and an increase in the number of bead defects forming along the electrospun nanofibres [12].

By studying the literature, some of which are presented above, it appeared that each polymer has different behaviour towards changing the operating parameters. Therefore, since no detailed study on PAN was carried out in this respect, in the present work, we have systematically evaluated the effects of operating parameters including electric voltage, solution feeding rate and tip-target distance on the morphology of electrospun PAN nanofibres.

EXPERIMENTAL

Materials

Industrial polyacrylonitrile (PAN) and dimethylformamide (DMF) were obtained from Iran Polyacryle Co. and Merck, respectively, as polymer and solvent. The weight average molecular weight ($\overline{M}_w$) and the number average molecular weight ($\overline{M}_n$) of the received



(a)

(b)

(c)

(d)

Figure 2. The images of initiating electrospinning jet and corresponding SEM images of the nanofibres produced from a 15 % wt PAN/DMF (tip-target distance 15 cm, feeding rate 2 mL/h). Voltage: (a) 9 kV; (b) 10 kV; (c) 11 kV; (d) 12 kV.

PAN were 100000 g/mol and 70000 g/mol, respectively. The polymer and solvent were dried before use. The 15 % wt solution of PAN in DMF was prepared at room temperature under constant mixing for ~2 h.

Electrospinning Set up

The electrospinning apparatus consists of a syringe pump with feeding rate from 0.1 mL/h to 60 mL/h, DC high voltage power supply and a grounded collector. Solution was loaded into a syringe and positive electrode was clipped onto the syringe needle having 0.7 mm outer diameter. The feeding rate of the polymer solution was controlled by syringe pump and solutions were electrospun horizontally onto the target.

Characterization

The morphology of electrospun PAN nanofibres was observed with a Philips scanning electron microscope (XL-30) after gold coating. The magnifications were 2500 and 5000. Optical micrographs were taken with a Sony digital handy cam (DCR-PC115E). The average diameter of the electrospun nanofibres was measured by analyzing SEM images with a custom code image analysis program.

RESULTS AND DISCUSSION

Effect of Voltage

Constant Feeding Rate

To investigate the effect of instability on the apex of the syringe needle which the electrospinnig jet originates, a series of experiments were carried out in which the applied voltage was varied from 9 to 12 kV, with constant feeding rate and tip-target distance of 2 mL/h and 15 cm, respectively. The images of the initiating jet from the apex of the syringe needle and the corresponding SEM images of nanofibres in these voltages are shown in Figure 2.

In the electrospinning, the electric current due to the ionic conduction of charge in the polymer solution is usually assumed small enough to be negligible. Therefore the only mechanism of charge transport is due to the flow of polymer from the tip of the needle to the grounded target. Thus, an increase in the electrospinning current generally causes an increase in the mass flow rate from the capillary tip to the grounded target when all other variables are held constant. Generally in the electrospinning systems, the spinning current has been found to increase with increasing voltage [12]. In these experiments, at 9 kV, a droplet of polymer solution remains suspended at the end of the syringe needle and the electrospinning jet originates from a stable cone at the bottom of the droplet. The diameter of this droplet is larger than the syringe needle diameter.

As the voltage is increased to 10 kV, the volume of the droplet decreases and the electrospinning jet originates from a stable cone at the bottom of the syringe needle. The nanofibres produced under these stable conditions have a uniform morphology and no bead defects were present.

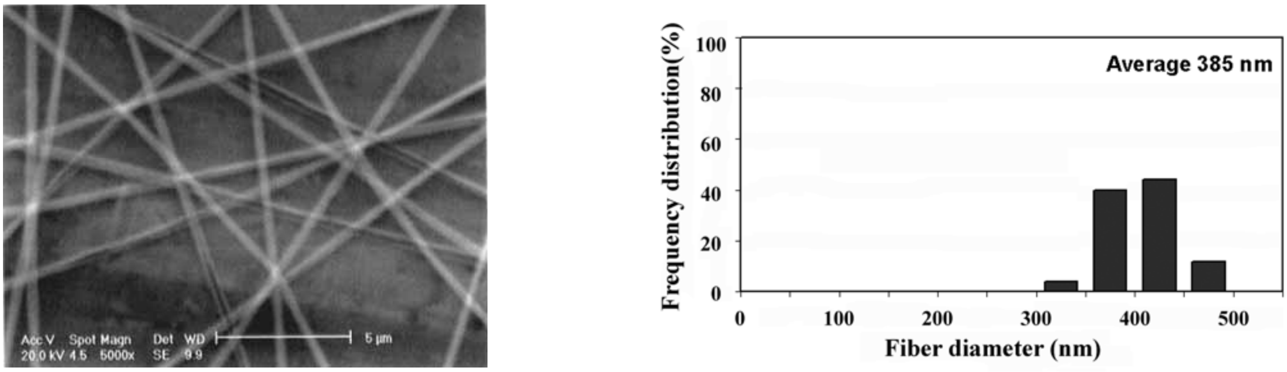
At voltage of 11 kV, the cone was receded and the jet originates from the liquid surface within the syringe needle tip. Still the electrospun nanofibres produced have essentially uniform morphology, but a few number of bead defect starts to appear in the nanofibre mat.

At 12 kV the solution jet appears to be initiating directly from the tip of needle with no externally visible droplet or cone. At this voltage, the jet moves around the edge of the syringe needle tip, indicating that the jet originates from the inside surface of the syringe needle, where the edge of the liquid surface meets the needle wall. The diameters of the nanofibres produced under this unstable condition, were not uniform and these nanofibres had many bead defects. The change in the shape of the liquid surface reflects a change in the mass balance that occurs at the end of the syringe needle tip.

Increasing the voltage further causes the rate at which solution is removed from the syringe needle tip to exceed the rate of delivery of solution to the tip needed to maintain the conical shape of the surface. This shift in the mass balance results in a sustained but increasingly less stable jet, as evidenced by the precession of the jet observed at 12 kV.

Variable Feeding Rate

A series of experiments were also carried out in which the applied voltage was varied from 10 to 20 kV and the tip to target distance was held at 15 cm. To obtain mass balance, the flow rate of the polymer solution to the needle tip was maintained in order to form an equilibrium Taylor cone.



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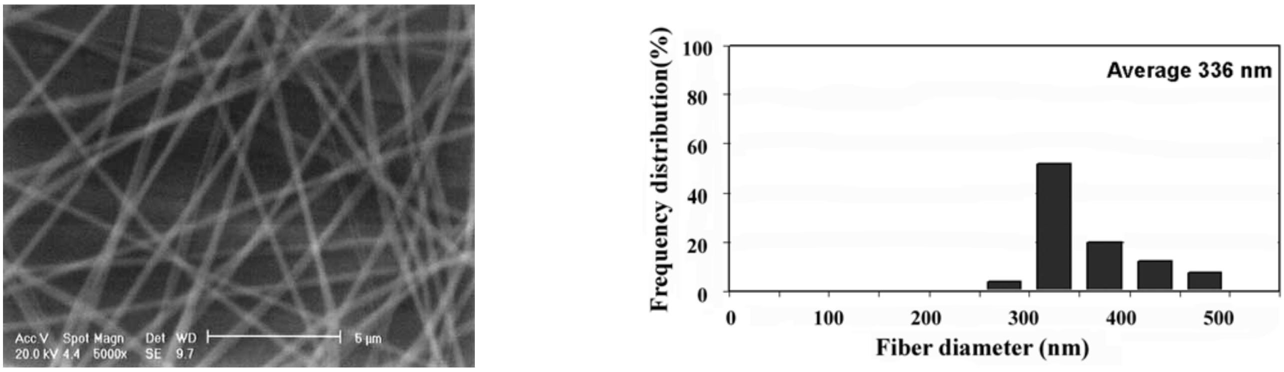

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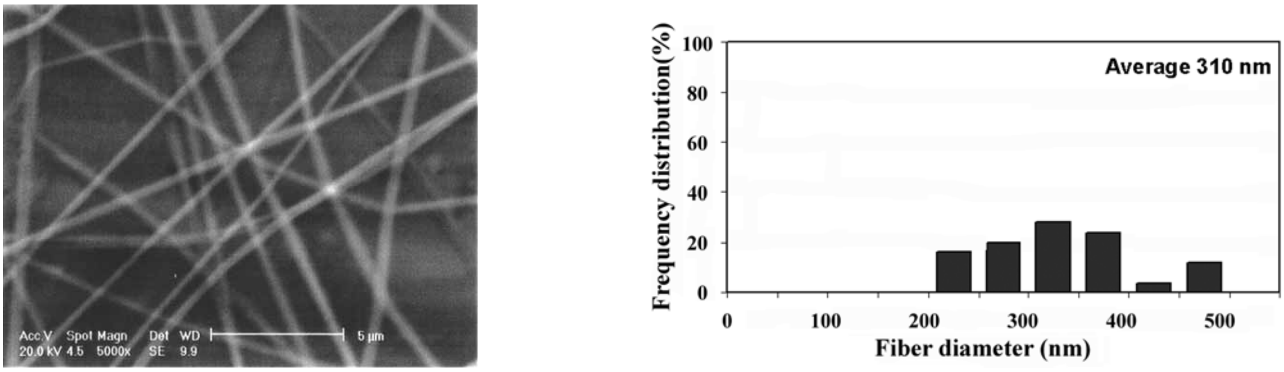

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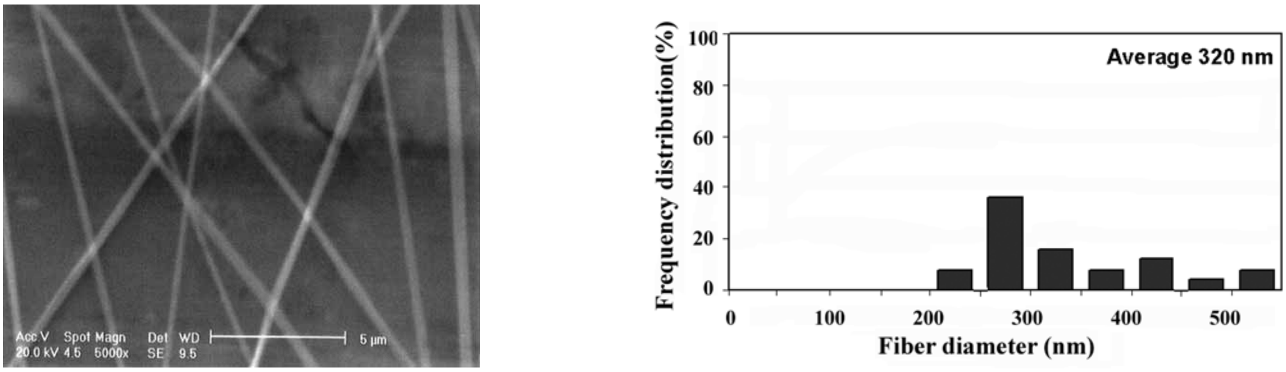

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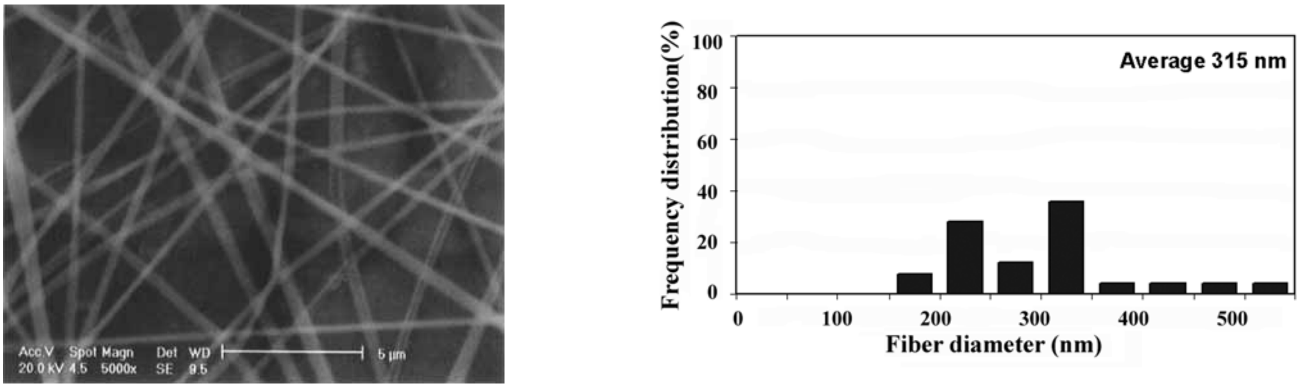


(e)

Figure 3. Effect of voltage on nanofibre diameter distribution from a 15 % wt PAN/DMF solution (tip-target distance: 15 cm). Voltage: (a) 10 kV; (b) 12.5 kV; (c)15 kV; (d) 17.5 kV; (e) 20 kV. Flow rate: (a) 2 mL/h; (b) 4 mL/h; (c) 6 mL/h; (d) 8 mL/h; (e) 12 mL/h.

As results are shown in Figure 3, there was a slightly decrease in the average diameter of nanofibres with increasing applied voltage. A considerable amount of very fine nanofibres with diameters below 250 nm were produced when the applied voltages were 15 kV and above. A narrow distribution of nanofibre diameters were observed at a lower voltages of 12.5-10 kV, while broader distribution in the fibre diameter was obtained at higher applied voltages of 15-20 kV.

With increasing the applied voltage, the electric field strength is also increased, so it will increase the electrostatic repulsive force on the fluid jet which favors the thinner fibre formation. On the other hand, the solution will be removed from the needle tip more quickly as the jet is ejected from Taylor cone. Therefore, the average diameters of the nanofibres are decreased with increasing applied voltage, but on the other hand broader distributions in the diameters of nanofibre were resulted at higher applied voltages.

Effect of Feeding Rate

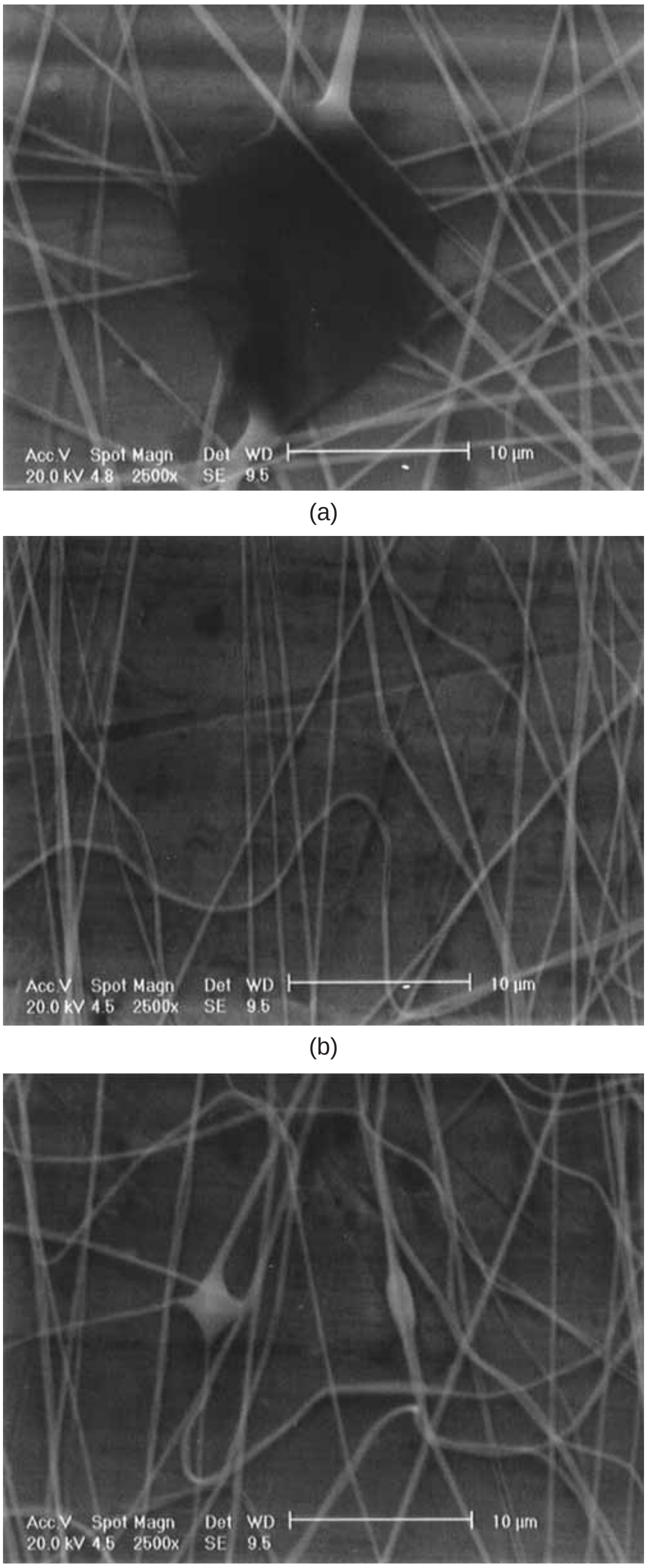
As mentioned earlier, a certain minimum value of the solution volume suspended at the end of the needle should be maintained in order to form an equilibrium Taylor cone. Therefore, different morphologies of electrospun nanofibres can be obtained with the change in feeding rates at a given voltage. Figure 4 shows the effect of the feeding rates on the morphology of the electrospun nanofibres from the 15 % wt PAN/DMF solution at different feeding rates and constant voltage of 10 kV.

At feeding rate of 4 mL/h, the feed exceeded the delivery rate of solution with applied electric forces. Therefore some of polymer solution is shot as tiny drops on to the collector and on the electrospun nanofibres mat. At lower feeding rate of 2 mL/h, a droplet of solution remains suspended at the end of the syringe needle and the electrospinning jet originates from a cone at the bottom of the droplet. The nanofibres produced under this condition have a uniform morphology and no bead defect was present. At lower feeding rate of 1 mL/h, the solution was removed from the needle tip by the electric forces, faster than the feeding rate of the solution onto the needle tip. This shift in the mass-balance resulted in sustained but unstable jet and nanofibres with beads were formed.

Effect of Tip to Target Distance

In this study, a series of experiments were carried out in which the distance of tip to target was varied from 5 to 15 cm. Results are shown in Figure 5.

One important physical aspect of the electrospun PAN nanofibres collected on the grounded collectors, is their dryness from the solvent used to dissolve the polymer, i.e., DMF. At the distances of tip to target of 5 and 7.5 cm, the structures of nanofibres were not completely stabilized and consequently the cross-sections of spun nanofibres became more flat and some nanofibres shuck together and bundles of nanofibres were collected. At the distances of tip to target of 15 cm and longer, the nanofibres exhibited a straight, cylindrical morphology indicating that the nanofibres are mostly dry when they have reached the target.

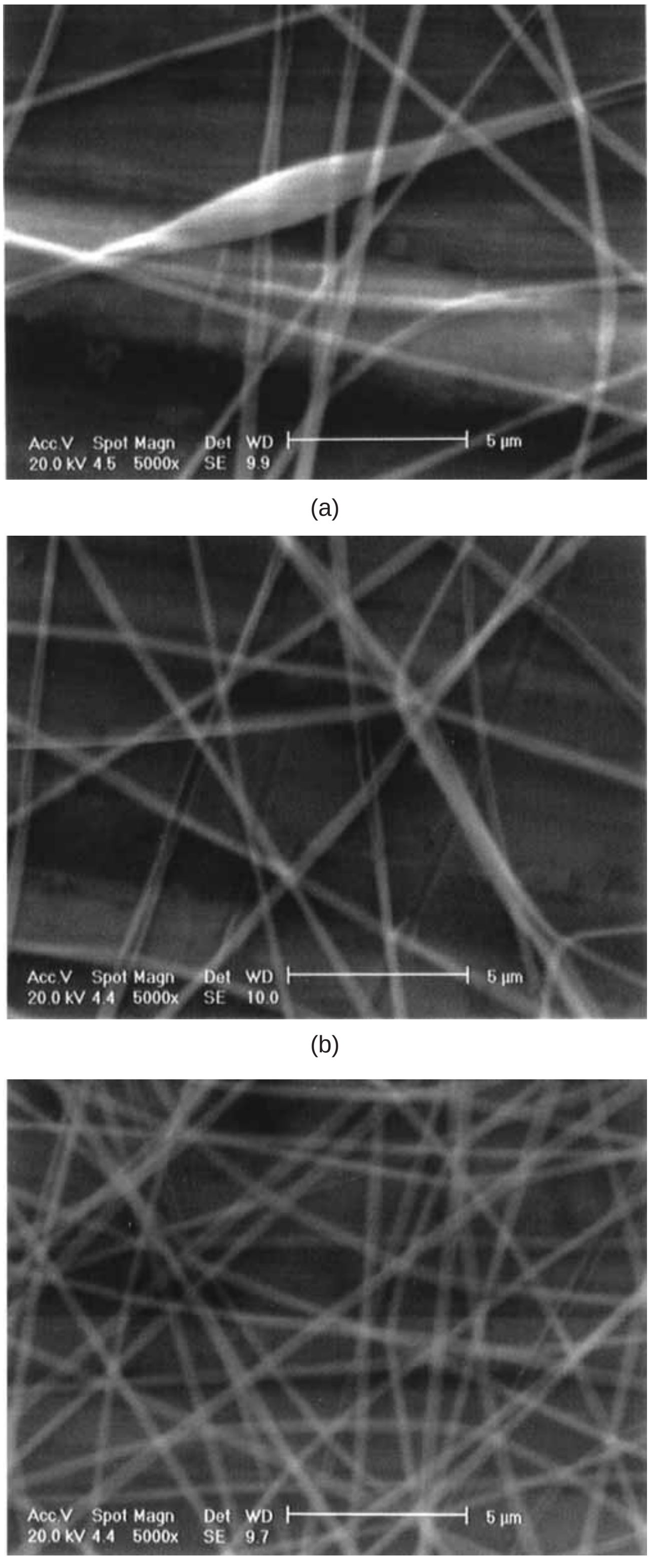


(a)

(b)

(c)

Figure 4. Effect of feeding rates of 15 % wt PAN/DMF solution on nanofibre morphology (voltage: 10kV, tip-target distance: 15cm). Feeding rate: (a) 4 mL/h; (b) 2 mL/h; (c) 1 mL/h.



(a)

(b)

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Figure 5. Effect of tip-target distance on fibre morphology from a 15 % wt PAN/DMF solution (voltage: 10kV, flow rate: 2 mL/h). Tip-target distance: (a) 5 cm; (b) 7.5 cm; (c) 15 cm.

CONCLUSION

In 15 % wt PAN/DMF solution, the average diameters of nanofibres decreased with increasing applied voltage from 10 to 20 kV, but broader distribution in the nanofibre diameter were obtained at 15 kV and above. At voltage of 10 kV, with 1 mL/h and 4 mL/h feeding rates, beaded nanofibres were collected, but with 2 mL/h feed rate, uniform nanofibres were obtained. At 5 and 7.5 cm tip-target distances, the structures of nanofibres were not completely stabilized, indicating that the nanofibres were mostly wet when they reached the target. But at 15 cm tip-target distance, the structure of nanofibres was completely dry and stabilized.

Our results have been showed that a certain minimum value of the solution volume suspended at the tip of the needle should be maintained in order to form an equilibrium Taylor cone.

REFERENCES

1. Horie K., Mita I., Kambe H., 1. Ziabicki A., *Fandamentals of Fibre Formation: The Science of Fibre Spinning and Drawing*, Wiley, New York (1976).
2. Doshi J., Reneker D.H., Electrospinning process and application of electrospun fibres, *J. Electrostatics.*, **35**, 151-160 (1995).
3. Reneker D.H., Yarin A.L., Fong H., Koombhongse S., Bending instability of electrically charged liquid jets of polymer solutions in Electrospinning, *J. Appl. Phys.*, **87**, 4531-4547 (2000).
4. Yarin A.L., Koombhongse S., Reneker D.H., Bending instability in electrospinning of nanofibres, *J. Appl. Phys.*, **89**, 3018-3026 (2001).
5. Fong H., Chun I., Reneker D.H., Beaded nanofibres formed during electrospinning, *Polymer*, **40**, 4585-4592 (1999).
6. Koski A., Yim K., Shivkumar S., Effect of molecular weight on fibrous PVA produced by electrospinning, *Mat. Letters.*, **58**, 493-497 (2004).
7. Son W.K., Youk J.H., Lee T.S., Park W.H., The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibres, *Polymer*, **45**, 2959-2966 (2004).
8. Son W.K., Youk J.H., Lee T.S., Park W.H., Electrospinning of ultrafine cellulose acetate fibres: Studies of a new solvent system and deacetylation of ultrafine cellulose acetate fibres, *J. Polym. Sci., Part B: Polym. Phsy.*, **42**, 5-11 (2004).
9. Wannatong L., Sirivat A., Supaphol P., Effects of solvents on electrospun polymeric fibres: Preliminary study on polystyrene, *Polym. Int.*, **53**, 1851-1859 (2004).
10. Jarusuwannapoom T., Hongrojjanawiwat W., Jitjaicham S., Wannatong L., Nithitanakul M., Pattamaprom C., Koombhongse P., Rangkupan R., Supaphol P., Effect of solvents on electro-spinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibres, *Eur. Polym. J.*, **41**, 409-421 (2005).
11. Zhang C., Yuan X., Wu L., Han Y., Sheng J., Study on morphology of electrospun poly(vinyl alcohol) mats, *Eur. Polym. J.*, **41**, 423-432 (2005).
12. Deitzel J.M., Kleinmeyer J., Harris D., Tan B., The effect of processing variables on the morphology of electrospun nanofibres and textiles, *Polymer*, **42**, 261-272 (2001).
13. Li D., Xia Y., Electrospinning of nanofibres: Reinventing the wheel?, *Adv. Mater.*, **16**, 1151-1170 (2004).
14. Frenot A., Chronakis I.S., Polymer nanofibres assembled by Electrospinning, *Curr. Opini. Coll. Interf. Sci.*, **8**, 64-75 (2003).