

Preparation of Poly(ether sulfone) Nanofibers by Gas-Jet/Electrospinning

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ABSTRACT: Poly(ether sulfone) (PES) nanofibers were prepared by the gas-jet/electrospinning of its solutions in *N,N*-dimethylformamide (DMF). The gas used in this gas-jet/electrospinning process was nitrogen. The morphology of the PES nanofibers was investigated with scanning electron microscopy. The process parameters studied in this work included the concentration of the polymer solution, the applied voltage, the tip-collector distance (TCD), the inner diameter of the needle, and the gas flow rate. It was found from experimental results that the average diameter of the electrospun PES fibers depended strongly on these process parameters. A decrease in the polymer concentration in the spinning solutions resulted in the formation of nanofibers with a smaller diameter. The use of an 18 wt % polymer solution yielded PES nanofibers with an average di-

ameter of about 80 nm. However, a morphology of mixed bead fibers was formed when the concentration of PES in DMF was below 20 wt % during gas-jet/electrospinning. Uniform PES nanofibers with an average diameter of about 200 nm were prepared by this electrospinning with the following optimal process parameters: the concentration of PES in DMF was 25 wt %, the applied voltage was 28.8 kV, the gas flow was 10.0 L/min, the inner diameter of the needle was 0.24 mm, the TCD was 20 cm, and the flow rate was 6.0 mL/h. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 909–917, 2008

Key words: electrospinning; fibers; nanotechnology; poly(ether sulfones)

INTRODUCTION

Poly(ether sulfone) (PES) is a kind of special engineering plastic with high performance and good processing characteristics. It has become an important separation-membrane material.¹ Therefore, PES and PES-based membranes with desired conductivities and selectivities have been prepared for widespread applications of gas and liquid separation in food, dairy, pharmaceutical, biochemical, water-treatment, fuel-cell, and other industries.^{2–14} In addition, PES membranes have been used for hemodialysis and hemodiafiltration because of their nontoxicity.^{15–18} Furthermore, in recent years, studies on the growth of human cells on PES hollow-fiber membranes have shown that PES fibers possess such broad human cell compatibility and positive biomaterial scaffold characteristics that this material could serve as a useful biomaterial in tissue engineering and biotechnology applications.^{19,20}

The study of nanofibers has been a subject of intensive research because of their unique properties and

widespread applications in many areas.^{21,22} Among the various methods used to prepare nanofibers, electrospinning has been very attractive in the past decade because it is a simple and versatile approach for producing a matrix of fibers with diameters ranging from a few nanometers to micrometers.^{23–29} To date, over 100 different polymers have been electrospun into nanofibers.²⁴ Because of the very high aspect ratio, specific surface area, and porosity, electrospun fibers are used for various applications, including tissue engineering,^{30–32} wound dressings,³³ drug delivery,^{34,35} and vascular grafts.^{36–38}

However, up to now, studies on PES electrospinning have hardly been reported. Zhu et al.³⁹ investigated only the relationship between the concentration of PES in *N,N*-dimethylformamide (DMF) and the diameter of electrospun PES fibers and showed that the fiber diameter increased with increasing polymer concentration. Park et al.⁴⁰ electrospun crystalline poly(L-lactic acid) and amorphous PES in mixed solvents.

Recently, in our laboratory, Yao et al.⁴¹ designed a gas-jet/electrospinning apparatus combining electrospinning with a gas-jet device and prepared polysulfone nanofibers with this equipment. Figure 1 shows their gas-jet/electrospinning apparatus. It is different from the standard electrospinning apparatus in the spinneret, in which the capillary of spinning fluid is circled by the tube of the gas jet (Fig. 2). Their experi-

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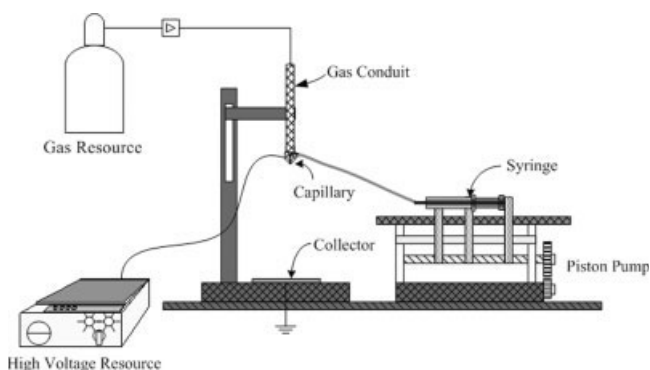


Figure 1 Schematic of the gas-jet/electrospinning equipment.

mental results show that gas-jet/electrospinning is a better method than conventional electrospinning, making finer and more uniform nanofibers and expressing higher efficiency in the electrospinning process.

In this work, the gas-jet/electrospinning of solutions of PES in DMF was completed, and nanometer fibers of PES were prepared. During the gas-jet/electrospinning, the effects of various process parameters on the diameter distribution of electrospun PES nanofibers were investigated.

EXPERIMENTAL

Materials

PES, the chemical structure of which is shown in Scheme 1, was obtained from Jida High Performance Materials Co., Ltd. (Changchun, Jilin Province, China), and its intrinsic viscosity was 0.37 dL/g in DMF at 298.2 K. DMF was an analytical reagent purchased from Chengdu Kelong Chemical Plant (Chengdu, Sichuan Province, China), and it was used without any further treatment.

Gas-jet/electrospinning

The PES solutions for gas-jet/electrospinning were prepared by the dissolution of the polymer in DMF at room temperature. The given concentrations of the prepared PES solutions were 10, 18, 20, 22, 25, and 27 wt %. The gas-jet/electrospinning was carried out in air (see Fig. 1). The spinning solution was placed in a syringe and was extruded to the spinneret fixed with a metal needle with an inner diameter of 0.24 or 0.27 mm. The tip of the needle was cut flat (see Fig. 2). The spinneret was connected to a high-voltage supply, which could generate direct-current voltages ranging from 26 to 45 kV. A piston pump was used to feed the polymer solution at the flow rate of 6.0 mL/h. A high voltage was applied to the spinneret, through which the polymer solution passed to be spun with the help

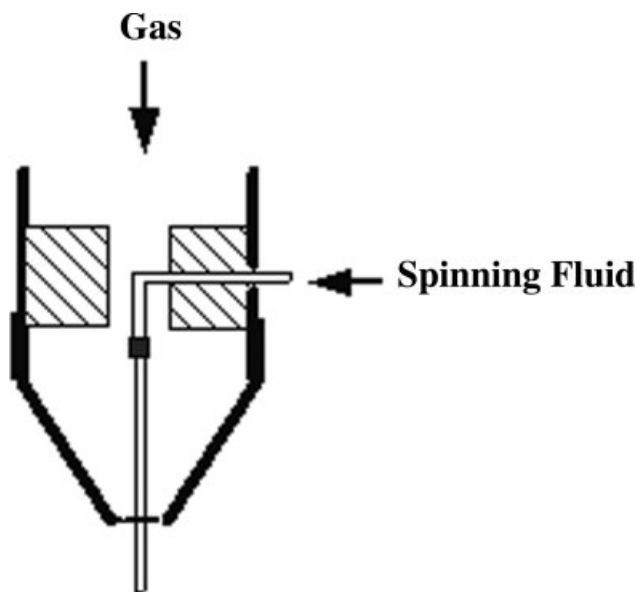


Figure 2 Schematic of the spinneret of the gas-jet/electrospinning equipment.

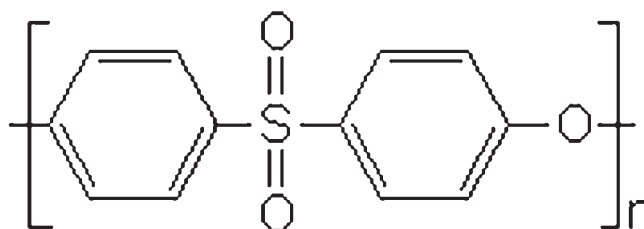
of an electrode. At the same time, nitrogen gas in storage was delivered through the pipe to the spinneret, and a gas jet occurred. The gas jet was ejected from the outer gas jacket. The fibers were collected on a clear stainless steel plate (the collector) connected to a ground under the spinneret. The applied voltages used in electrospinning were 27.7, 28.2, 28.8, 29.2, and 29.7 kV. The tip-collector distances (TCDs) were 10, 15, 20, 25, and 30 cm. The gas flow rates were 5.0, 7.5, 10.0, 12.5, and 15.0 L/min, and they were controlled by a gas flow meter.

Scanning electron microscopy (SEM) characterization

The photographs of the electrospun nanofibers were obtained by a JEOL JSM-5900LV scanning electron microscope (Japan). The average diameter of the PES nanofibers was measured by SigmaScan Pro 2.0 software (Systat Software Inc.) from the SEM photographs.

RESULTS AND DISCUSSION

In this work, the following process parameters were examined in detail: the solution concentration, the



Scheme 1 Chemical structure of PES.

applied voltage, the TCD, the inner diameter of the needle, and the gas flow rate. Their relationships with the average diameters of the PES nanofibers are summarized and discussed.

Solution concentration

It was found experimentally that the morphology of the obtained PES nanofibers obviously changed when the solution concentration of PES in DMF was increased from 10 to 27 wt % (Fig. 3). The other process parameters were as follows: the voltage was 28.8 kV, the gas flow rate was 10.0 L/min, the inner diameter of the metal needle was 0.24 mm, the TCD was 20 cm, and the solution flow rate was 6.0 mL/h. When the concentration was 10 wt %, the PES solution was electrostatically sprayed to form many spherical beads with different diameters instead of being gas-jet/electrospun to obtain fibers.

When the concentration was increased (at 18 and 20 wt %), the nanofibers were obtained, and the amount of the spherical beads remarkably decreased. Generally, a bead-fiber morphology is formed during the electrospinning of many polymers under certain conditions, especially at a low polymer concentration. For example, Fong et al.⁴² found that in the electrospinning of poly(ethylene oxide) and water, bead fibers were generally obtained at lower concentrations. It was reasonable that the morphology of the mixed bead fibers would be formed when the concentration of PES in DMF was below 20 wt % under these conditions.

As the concentration was increased to 22, 25, and 27 wt %, uniform nanofibers were obtained. However, a further increase in the polymer concentration was impracticable. Hal et al.⁴³ studied the effect of the PES concentration on flat and hollow-fiber membrane performances. They found that there is a critical concentration, above which a small addition of the polymer to the solution causes a large viscosity increase because polymer-polymer contacts are inevitable. The concentration of 30 wt % may be beyond the critical concentration. Therefore, it is natural that the gel appeared apparently during the dissolution of PES at this concentration, and it could not be suitable to carry out any electrospinning.

The relationships between the average diameters of PES nanofibers and the solution concentrations of PES in DMF are shown in Figure 4(a). The average diameters of the nanofibers increased gradually from 83 to 287 nm, and the diameter distributions of those fibers widened, as the concentration of the PES solution increased from 18 to 27 wt %.

Applied voltage

Figure 5 shows SEM images and diameter distributions of the PES nanofibers gas-jet/electrospun from

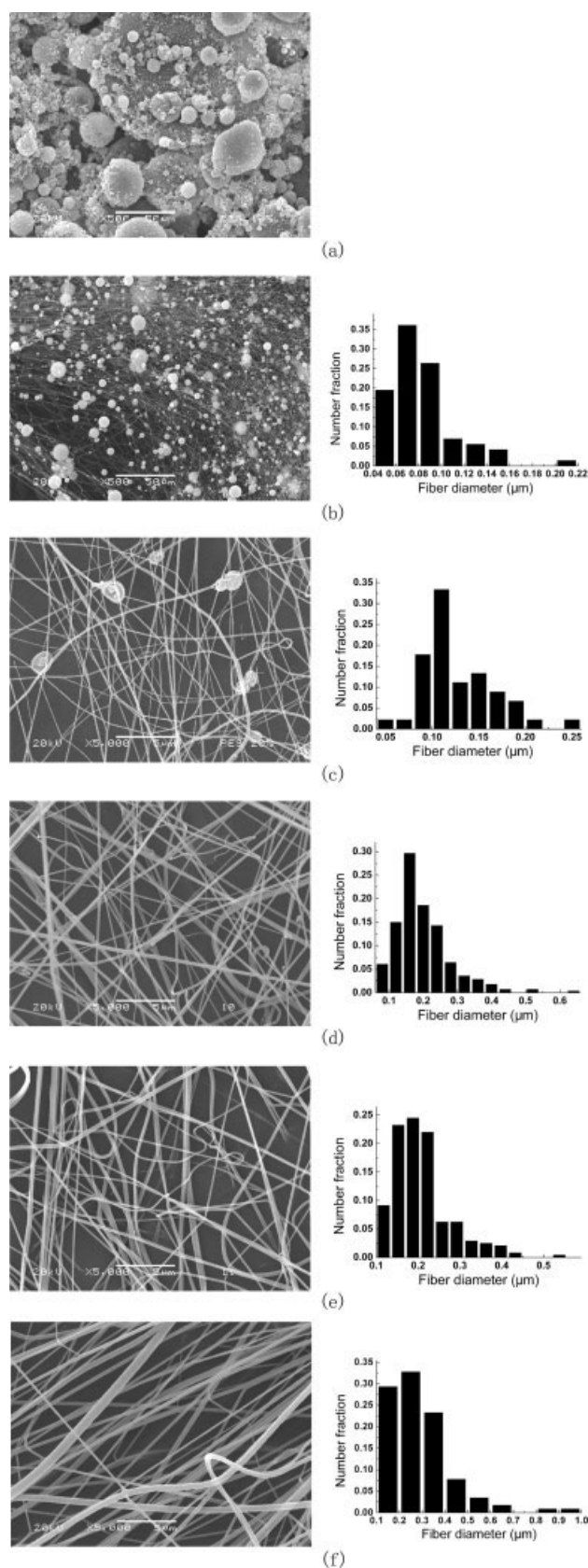


Figure 3 SEM images and diameter distributions of PES fibers gas-jet/electrospun from (a) 10, (b) 18, (c) 20, (d) 22, (e) 25, and (f) 27 wt % PES solutions. The original magnifications were (a) 500 \times and (b–f) 5000 \times .

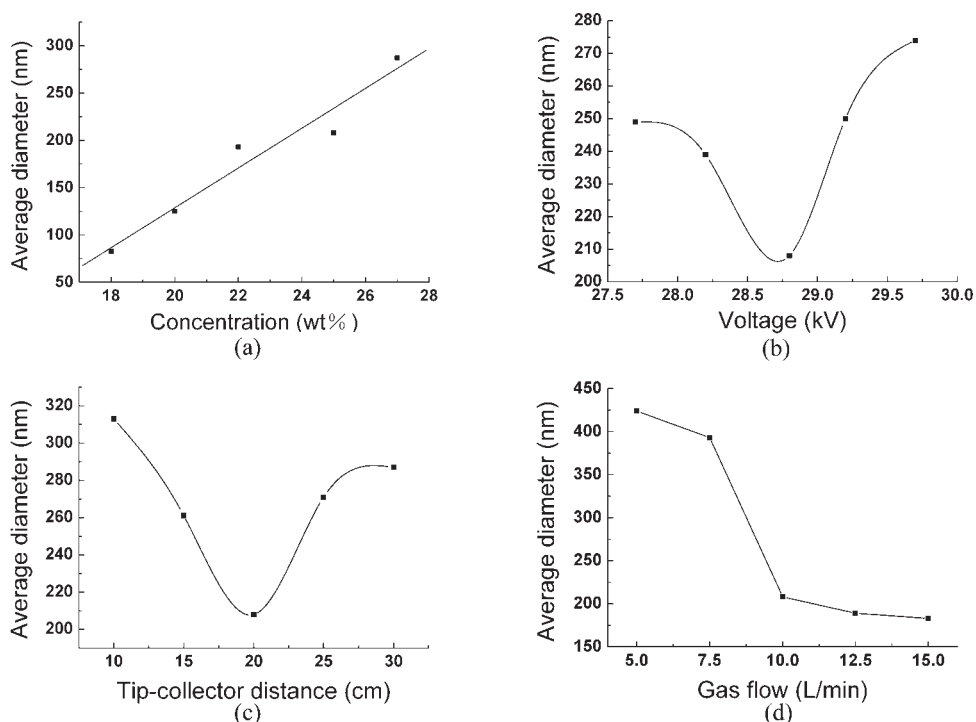


Figure 4 Dependence of the average diameters of gas-jet/electrospun PES nanofibers on the process parameters.

25 wt % solutions of PES in DMF at the applied voltages of 27.7, 28.2, 28.8, 29.2, and 29.7 kV. In the gas-jet/electrospinning, the other process parameters were as follows: the gas flow rate was 10.0 L/min, the inner diameter of the metal needle was 0.24 mm, the TCD was 20 cm, and the solution flow rate was 6.0 mL/h. It was shown that uniform nanofibers could be obtained under these conditions (see Fig. 5). Figure 4(b) shows the effect of the applied voltage on the average diameter of gas-jet/electrospun nanofibers. It can be concluded from Figure 4(b) that the average diameters of these nanofibers were reached at a minimum value after an initial increase in the applied voltage from 27.7 to 28.8 kV and then became larger as the applied voltage increased from 28.8 to 29.7 kV. This result agreed with the electrospinning results of acrylic microfibers by Baumgarten⁴⁴ and those of poly (D,L-lactic acid) by Zong et al.⁴⁵ Generally, it has been accepted that a higher applied voltage leads to a stronger electrostatic force and greater splittability of the droplet, which results in a decrease in the average diameters of these electrospun fibers. Therefore, the average diameters of these fibers decreased after an initial increase in the applied voltage. On the other hand, the flight time of electrospinning nanofibers in the electrostatic field also decreased with increasing voltage, and this led to a shorter deformation time to form nanofibers. As a result, electrospun nanofibers formed with greater diameters. When the effect of the shorter flight time was beyond the effect of the

greater electrostatic force, the average diameter increased with the increase in the applied voltage. These two opposite effects led to the minimum value of the average diameter with increasing applied voltage [see Fig. 4(b)].

TCD

Figure 6 shows SEM images and diameter distributions of PES nanofibers prepared at TCDs of 10, 15, 20, 25, and 30 cm. The concentration of the spinning solution of PES in DMF was 25 wt %. The other process parameters were as follows: the applied voltage was 28.8 kV, the gas flow rate was 10.0 L/min, the inner diameter of the metal needle was 0.24 mm, and the solution flow rate was 6.0 mL/h. No obvious morphological changes were found with the change in TCD. The average diameters of the fibers decreased with increasing TCD at the beginning of the curve in Figure 4(c). The increase in TCD could give a longer flight time to evaporate the solvent and to split the charged filaments of the fluids. On the other hand, the decrease in the electrostatic force and the splittability of the droplet resulted because of the increasing TCD at a fixed voltage. Therefore, the total effect of TCD on the average diameter of the fibers was similar to that of the applied voltage. That is, the average diameters of these nanofibers reached a minimum value after an initial increase at TCD and then became larger with increasing TCD, as shown in Figure 4(c).

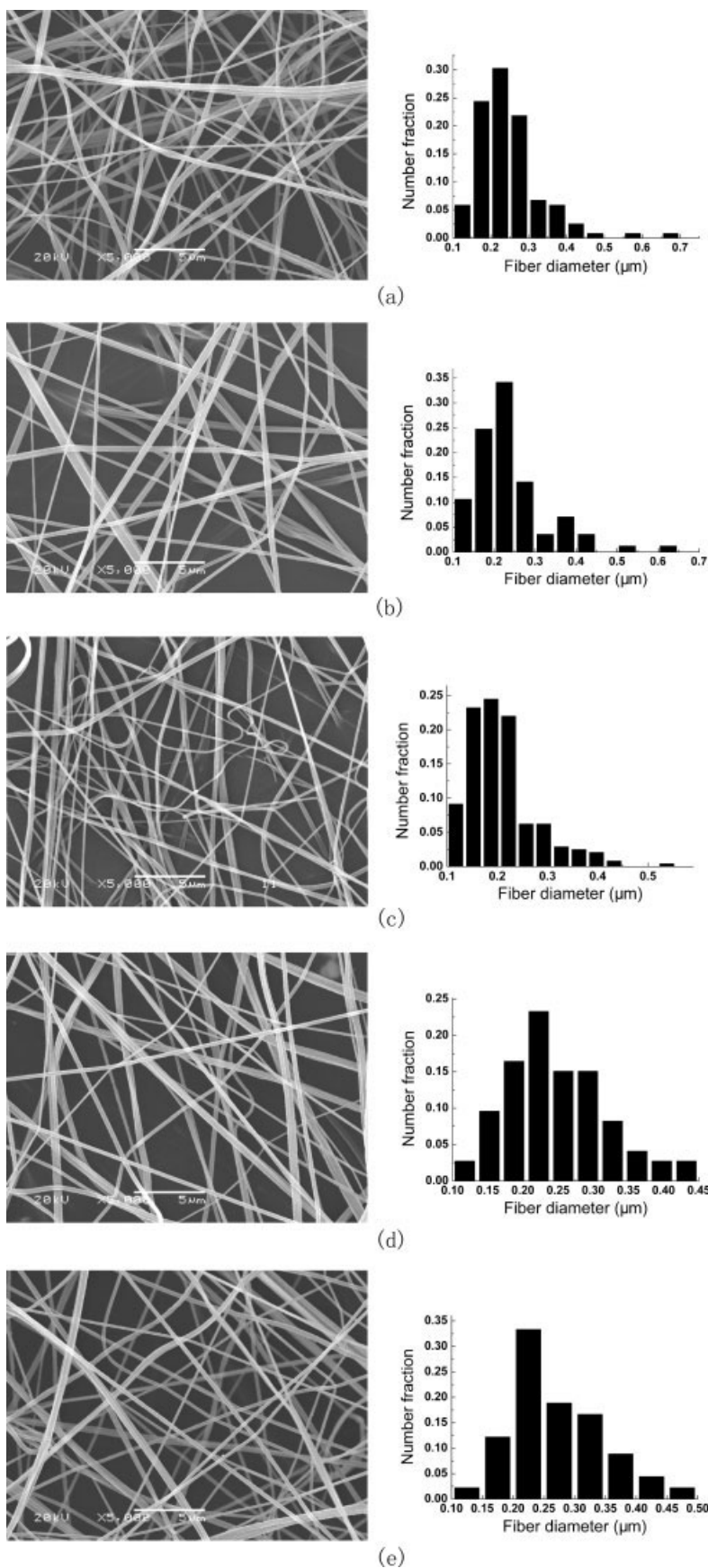


Figure 5 SEM images and diameter distributions of PES nanofibers gas-jet/electrospun at applied voltages of (a) 27.7, (b) 28.2, (c) 28.8, (d) 29.2, and (e) 29.7 kV (original magnification = 5000×).

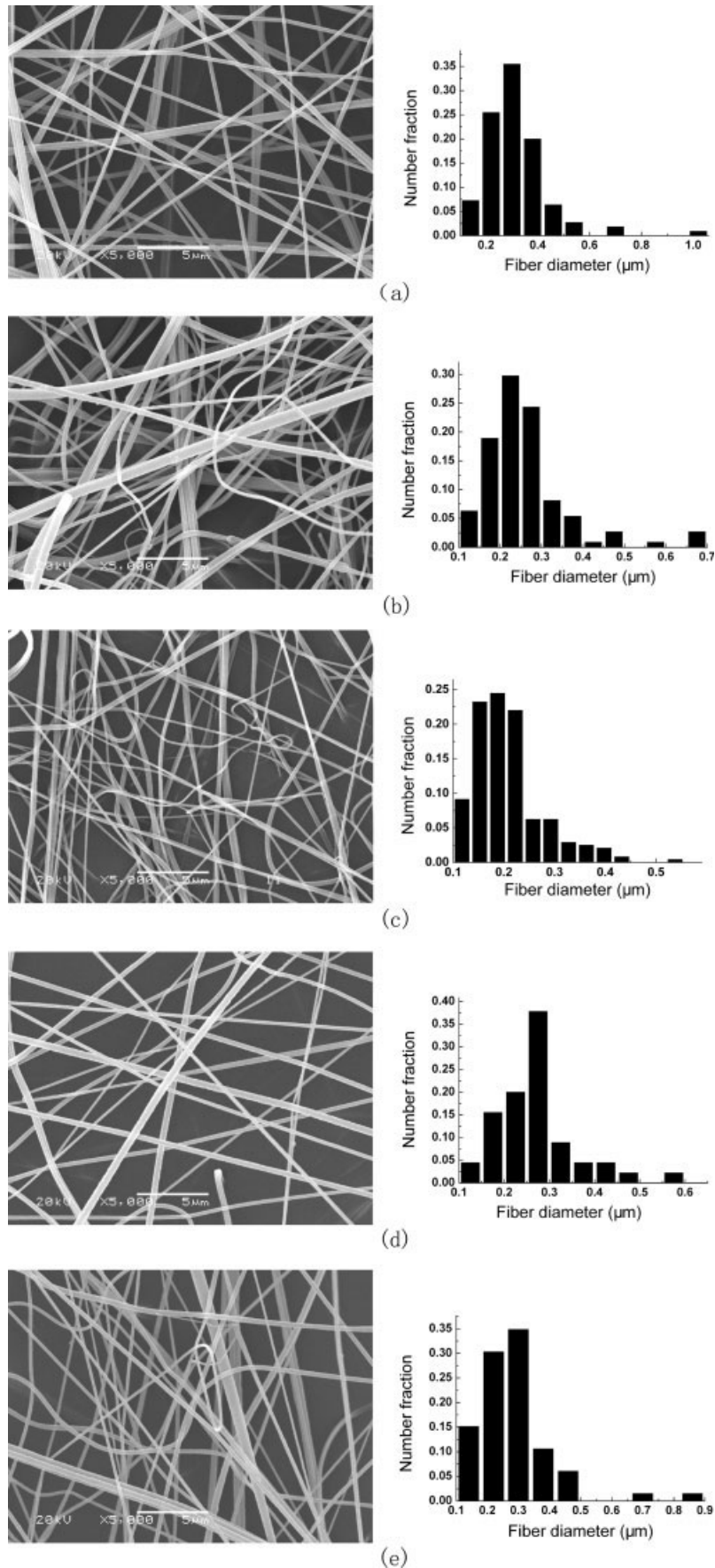


Figure 6 SEM images and diameter distributions of PES nanofibers gas-jet/electrospun at TCDs of (a) 10, (b) 15, (c) 20, (d) 25, and (e) 30 cm (original magnification = 5000 \times).

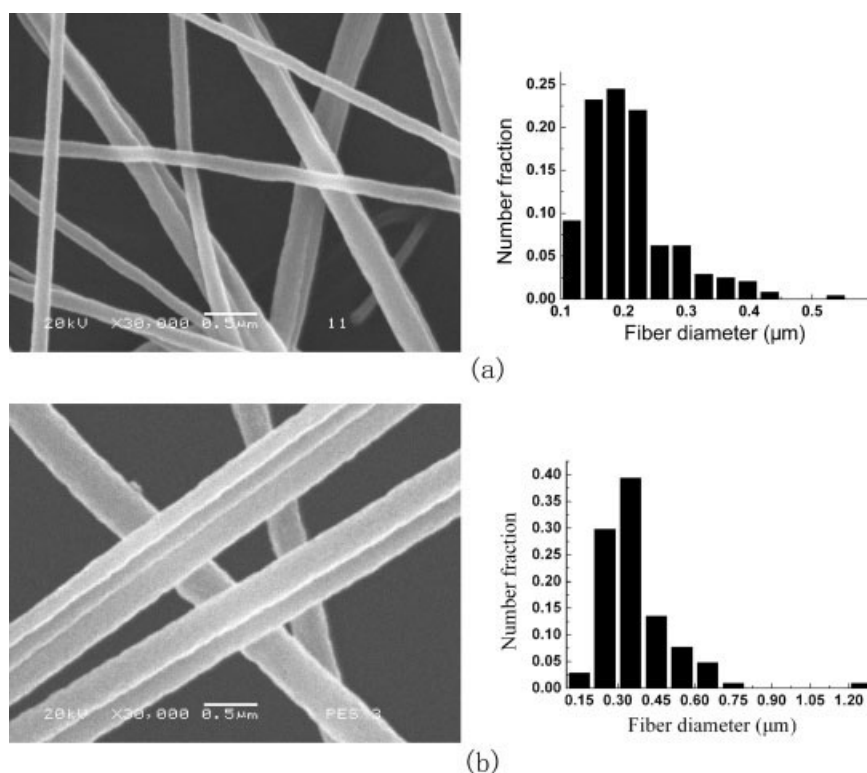


Figure 7 SEM images and diameter distribution of PES nanofibers gas-jet/electrospun at inner diameters of the metal needle equal to (a) 0.24 and (b) 0.27 mm (original magnification = 30,000 \times).

Inner diameter of the needle

Figure 7 shows SEM images and diameter distributions of the PES fibers gas-jet/electrospun from 25 wt % solutions of PES in DMF. The inner diameter of the metal needle was 0.24 or 0.27 mm. The other process parameters were as follows: the applied voltage was 28.8 kV, the gas flow rate was 10.0 L/min, the TCD was 20 cm, and the solution flow rate was 6.0 mL/h. The average diameters of these nanofibers were 208 and 365 nm when the inner diameters of the metal needle were 0.24 and 0.27 mm, respectively. It was assumed that the smaller inner diameter of the needle caused a smaller drop, which was easy to split.

Gas flow rate

The main difference between gas-jet/electrospinning and standard electrospinning is that the additional drawing action of the gas jet acts on the polymer fluid jet during the electrospinning process.⁴¹ Figure 8 shows SEM images and diameter distributions of PES fibers gas-jet/electrospun from 25 wt % solutions of PES in DMF. The gas flow rates were 5.0, 7.5, 10.0, 12.5, and 15.0 L/min. The other process parameters were as follows: the applied voltage was 28.8 kV, the inner diameter of the metal needle was 0.24 mm, the TCD was 20 cm, and the solution flow rate was 6.0 mL/h. The experimental results showed that the

average diameters of the PES fibers decreased monotonically as the gas flow rate increased. When the gas flow rate was increased from 5.0 to 7.5 L/min, the average diameter of the fibers decreased slightly from 424 to 393 nm. However, as the gas flow increased from 7.5 to 10.0 L/min, the average diameter of the fibers decreased remarkably from 393 to 208 nm. As the gas flow was further increased, the average diameter of the fibers decreased only slightly from 208 nm to 183 nm, as shown in Figure 4(d). It was confirmed that the additional drawing action of the gas jet on the polymer fluid jet played an important role during the spinning process.

CONCLUSIONS

Nanofibers of PES were prepared by the gas-jet/electrospinning of PES/DMF solutions. It was suggested on the basis of the experimental results that the solution concentration, the inner diameter of the needle, and the gas flow rate were the most important process parameters influencing the morphology and average diameters of the gas-jet/electrospun nanofibers. A decrease in the polymer concentration in spinning solutions resulted in the formation of nanofibers with a smaller diameter. The use of an 18 wt % polymer solution gave PES nanofibers with an average diameter of about 80 nm. However, a morphology of mixed bead

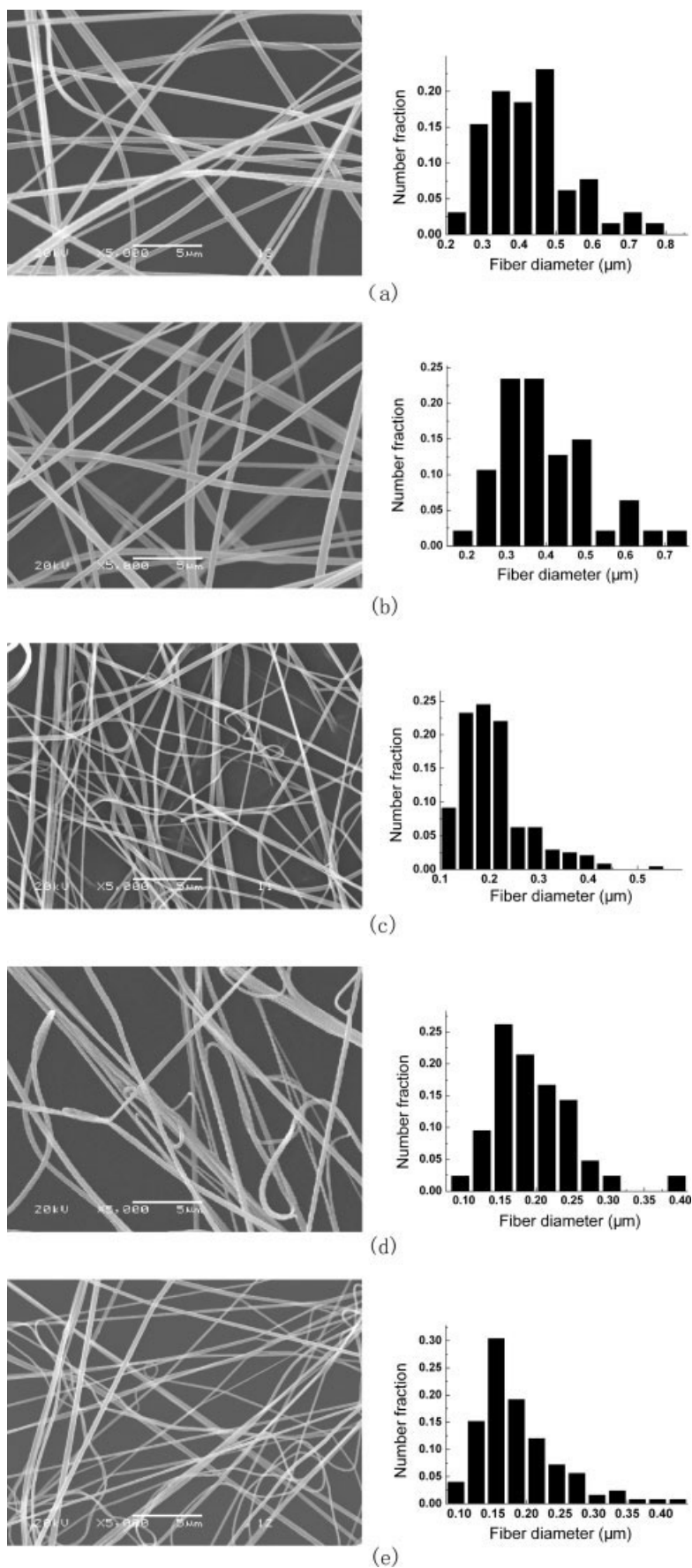


Figure 8 SEM images and diameter distributions of PES nanofibers gas-jet/electrospun at gas flow rates of (a) 5.0, (b) 7.5, (c) 10.0, (d) 12.5, and (e) 15.0 L/min (original magnification = 5000 \times).

fibers was formed when the concentration of PES in DMF was below 20 wt % during gas-jet/electrospinning. The smaller insider diameter of the capillary and the larger gas flow rate led to nanofibers with a smaller diameter. Typically, uniform PES fibers with an average diameter of about 200 nm were prepared by gas-jet/electrospinning with the following process parameters: the concentration of PES in DMF was 25 wt %, the applied voltage was 28.8 kV, the gas flow rate was 10.0 L/min, the inner diameter of the metal needle was 0.24 mm, the TCD was 20 cm, and the solution flow rate was 6.0 mL/h.

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