

Morphology of ultrafine polysulfone fibers prepared by electrospinning

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Abstract: Ultrafine fibers of bisphenol-A polysulfone (PSF) were prepared by electrospinning of PSF solutions in mixtures of *N,N*-dimethylacetamide (DMAC) and acetone at high voltages. The morphology of the electrospun PSF fibers was investigated by scanning electron microscopy. Results showed that the concentration of polymer solutions and the acetone amount in the mixed solvents influenced the morphology and the diameter of the electrospun fibers. The processing parameters, including the applied voltage, the flow rate, and the distance between capillary and collection screen, were also important for control of the morphology of electrospun PSF fibers. It was suggested that uniform ultrafine PSF fibers with diameter of 300–400 nm could be obtained by electrospinning of a 20 % (wt/v) PSF/DMAC/acetone (DMAC:acetone = 9:1) solution at 10–20 kV voltages when the flow rate was 0.66 ml h⁻¹ and capillary–screen distance was 10 cm.

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Keywords: electrospinning; ultrafine fiber; polysulfone; morphology; diameter; fibers

INTRODUCTION

Electrospinning, also known as electrostatic spinning, is an important method for preparing ultrafine fibers. Diameters of such electrospun fibers ranging from less than 100 nm to over 1 µm have been reported.^{1–3} In a typical electrospinning process, a high voltage in the range 5–30 kV is applied to the polymer solution, which is held in a medical syringe equipped with a capillary of about 1 mm in diameter.^{1,4} The high-voltage supply is connected to the metal capillary by a copper wire. During the electrospinning, ultrafine fibers are collected on stationary or revolving grounded metallic targets.^{1,4} In the high-voltage electric field between the metal capillary and the collection target, the droplet of the polymer solution at the capillary tip is distorted into a cone, called a Taylor cone.⁵ When the voltage exceeds a critical value, the charged droplet can overcome its own surface tension and viscoelasticity to form a jet. The jet is stretched and accelerated in the electric field and undergoes a whipping instability to split into ultrafine fluids.⁶ Evaporation of solvent makes the fluids solidify and form ultrafine fibers.^{3,5,6} Non-woven fibrous membranes can be directly collected on the target, which is also called a collection screen.^{4,7}

It has been known for almost 100 years that polymer fibers can be prepared from polymer solutions or polymer melts with the help of an electrical supply. In 1934, Formhals invented

the setup of electrospinning.⁸ In recent years, Reneker and co-workers investigated the electrospinning of over 30 different kinds of polymers and characterized the physical properties of electrospun fibers.^{3,5,9,10}

Many polymers have been electrospun in solutions, such as poly(ethylene oxide) in water,¹ polyurethane in *N,N*-dimethylformamide (DMF),¹¹ poly-L-lactide in dichloromethane,¹² nylon 6 in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) or in an HFIP and DMF mixture,¹³ poly(ϵ -caprolactone) in methylene chloride (MC), an MC and DMF mixture or an MC and toluene mixture,⁷ and so on. Natural proteins such as silk fibroin^{14,15} and collagen¹⁶ have also been processed by electrospinning to generate nanofibers. Generally, for most polymers, electrospun fibers are more easily prepared in solution than in the melt. During solution electrospinning, mixed solvents have often been applied.^{7,13} Melt electrospinning of polyethylene, polypropylene and aromatic polyesters has also been studied.^{17,18}

In the past two years, electrospinning has become more and more attractive in many areas. Because of their small size and high porosity, electrospun fibers have high specific surface areas. The nature of the ultrafine electrospun fibers is different from the polymer itself so that the ultrafine fibers or membranes exhibit a variety of potential applications, including nanocomposites,¹³ high-performance

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filters^{19,20} and functional coatings.²¹ Ultrafine fibers or mats electrospun from biodegradable polymers such as polylactide,^{4,22–25} polyglycolide²⁶ and their copolymers,²⁷ and poly(ϵ -caprolactone)²⁸ could be applied as tissue-engineering scaffolds,^{26–28} controlled-release carriers^{4,22} and nanotemplates.^{23,24}

Many factors influence the electrospinning process, including the nature of the polymer itself (relative molar mass and its distribution), the properties of the polymer solutions (concentration, viscosity, conductivity and surface tension), and the process parameters (applied voltage, flow rate, distance between capillary tip and collection screen, temperature and humidity in the environment).^{6,29–32} Among these factors, the properties of the polymer solutions are the most important, and these are mainly determined by the solvent or mixed solvents and their mixing ratios, in addition to the polymer nature.

In this paper, electrospinning of bisphenol-A polysulfone (PSF) was studied because of its low price and good solubility. It can be considered as a model polymer for examining the electrospinning process.

EXPERIMENTAL

Materials

Bisphenol-A polysulfone (denoted as polysulfone, PSF) with an inherent viscosity of 0.6 dl g^{-1} was supplied by Beijing Dongfang Chemical Engineering Factory (China). The solvents *N,N*-dimethylacetamide (DMAC) and acetone were chemical reagents.

Preparation and properties of the electrospun solutions

The PSF solutions for electrospinning were prepared by dissolving the polymer in a mixture of DMAC and acetone in given ratios at room temperature. The polymer concentration was determined by the percentage of PSF (g) in the solvent (ml). Two series of PSF solutions were prepared for the study (Table 1), one was PSF solutions with different concentrations in a mixed solvent of DMAC and acetone in a 9:1 ratio (Samples 1–5), the other was PSF solutions with the same concentration in mixed solvents of different DMAC to acetone ratios (Samples A–D).

The surface tension of the electrospun PSF solutions was tested by the Wilhelmy plate method with a tensiometer (DCAT 21, Dataphysics, Germany)

Table 1. The properties of PSF solutions for electrospinning

Sample number	Solution contents			Solution properties		
	PSF (g)	DMAC (ml)	Acetone (ml)	Viscosity (Pa s)	Surface tension (mN m^{-1})	Conductivity ($\mu\text{S cm}^{-1}$)
1	8	90	10	0.021	34.68	13
2	10	90	10	0.039	34.74	38
3	12	90	10	0.072	35.11	40
4	15	90	10	0.182	35.28	46
5	20	90	10	0.520	35.47	40
A	20	100	0	0.548	37.11	44
B	20	90	10	0.520	35.47	40
C	20	80	20	0.650	33.81	28
D	20	70	30	0.730	32.56	21

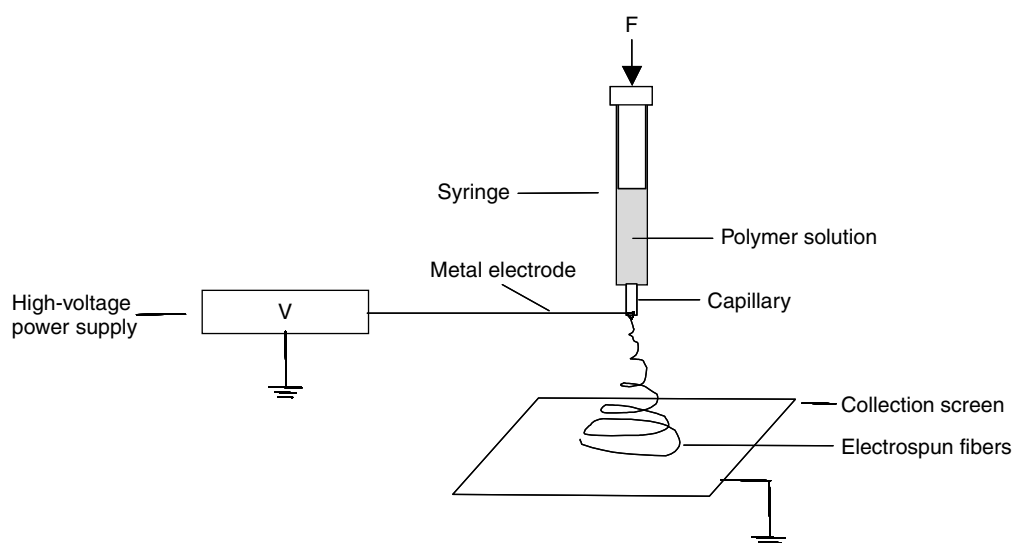
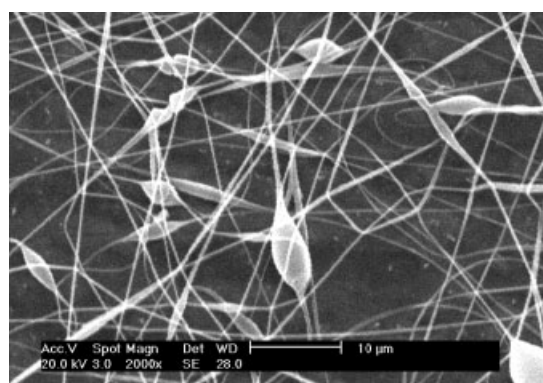
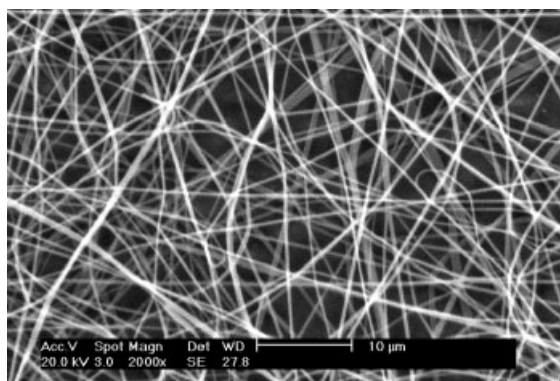


Figure 1. Schematic setup of electrospinning.

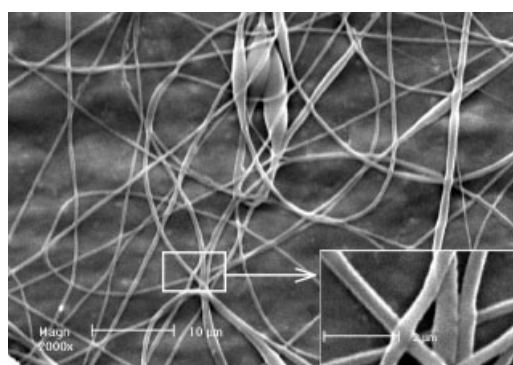


a

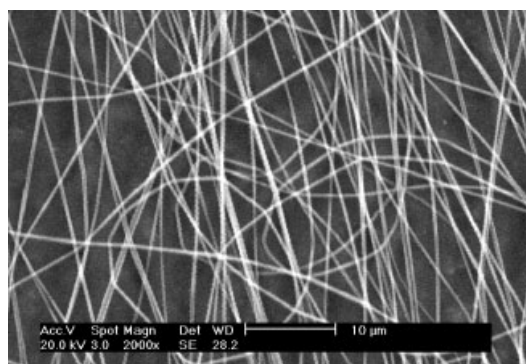


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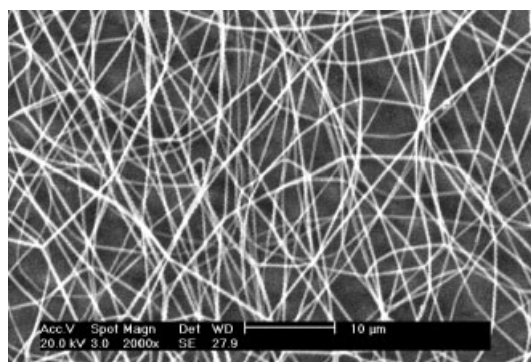
Figure 2. SEM micrographs of ultrafine PSF fibers electrospun from (a) 12 % and (b) 15 % PSF solutions in DMAC/acetone (9:1) mixed solvent at 10 kV; flow rate = 0.40 ml h^{-1} , capillary–screen distance = 10 cm. (Original magnification: 2000 \times).



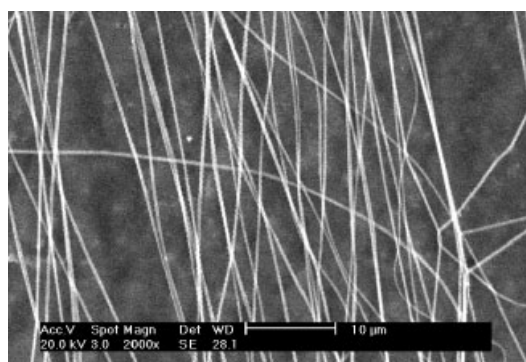
a



b



c



d

Figure 3. Effect of the acetone amount in the mixed solvent on the morphology of electrospun PSF ultrafine fibers. Solution concentration = 20 %; voltage = 10 kV; flow rate = 0.66 ml h^{-1} ; capillary–screen distance = 10 cm. The ratios of DMAC to acetone are (a) 10:0, (b) 9:1, (c) 8:2 and (d) 7:3. (Original magnification: 2000 \times , larger magnification of the boxed area: 10 000 \times).

at room temperature. The clear platinum plate was used. The viscosity of polymer solutions was measured in a rotating viscometer (Model NDJ-79, Shanghai, China). The electrical conductivity of polymer solutions was determined in a conductivity instrument (Model DDS-11A, Shanghai, China).

Electrospinning

The electrospinning was carried out in air. The setup is shown in Fig 1. The polymer solution was contained in a medical syringe fixed with a size 12 metal needle with inner diameter of 0.8 mm. The tip of the needle had been cut flat. The metal capillary was connected to a high-voltage supply, which could generate DC voltages up to 60 kV. The ultrafine fibers were collected on a flat aluminium foil (collection screen) connected to ground under the syringe. The flow rate of the solution was controlled by placing various masses of weights on the top of the syringe piston. The corresponding average flow rate was calculated from the total mass of the vacuum-dried electrospun fibrous membranes, the polymer concentration and the electrospun time from 8–11 tests.

Characterization

The morphology of the electrospun ultrafine fibers was observed under a scanning electron microscope (SEM) (Philips XL-30) after gold coating. The average fiber diameter (AFD) of the electrospun fibers was measured by Adobe Photoshop 5.0 software from the

SEM pictures at original magnification of $10\,000\times$ (not shown in this paper).

RESULTS AND DISCUSSION

According to Fong *et al.*,²⁹ the properties of polymer solutions (including surface tension, viscosity and conductivity) could have effects on the morphology of the electrospun fibers. These system parameters are dependent on the solution concentration and the nature of the solvent. The process parameters, such as the applied voltage, the flow rate and the capillary–screen distance, would also influence the morphology of the electrospun fibers. In this study, the effects of the polymer concentration, the DMAC to acetone ratio, the applied voltage, the flow rate and the capillary–screen distance were investigated in detail.

From the solution properties shown in Table 1, the viscosity of PSF solutions increased sharply from 0.021 Pa s to 0.520 Pa s with the increase of the polymer concentration from 8 % to 20 % (Samples 1–5). The increase of the acetone amount from 0 % to 30 % in the mixed solvent also made the solution viscosity increase significantly (Samples A–D). The surface tension of the PSF solutions exhibited a slight increase with increasing concentration and showed obvious decrease with the addition of acetone. The conductivity of the PSF solutions also showed a tendency to increase with the concentration increase, but decreased sharply with the increase of the acetone amount.

Solution concentration

Figure 2 shows SEM micrographs of the ultrafine fibers electrospun from 12 % and 15 % PSF solutions in the DMAC/acetone (9:1) mixed solvent at 10 kV when the flow rate was 0.40 ml h^{-1} and the capillary–screen distance was 10 cm. The electrospun fibers exhibited bead-fiber morphology when the concentration was 12 %, but better-defined ultrafine fibers were obtained when the concentration was increased to 15 %. The AFD in the latter case was $365 \pm 31\text{ nm}$ ($n = 10$). According to the results of Fong *et al.* in the electrospinning of poly(ethylene oxide) (PEO)/water, bead-fibers were generally obtained at lower concentrations because of the lower solution viscosity.²⁹ It could be concluded that the bead-fiber morphology would form when the PSF concentration was below 12 % under the same conditions. On the other hand, uniform ultrafine fibers would be generated by electrospinning of the PSF/DMAC/acetone (DMAC/acetone = 9:1) solutions in at least 15 % concentration. The lower viscosity and conductivity of the lower concentration PSF solutions (Table 1) could be the possible reasons leading to bead-fiber morphology.

Acetone amount in the mixed solvent

SEM micrographs of the ultrafine fibers electrospun from 20 % PSF solutions in the mixed solvents

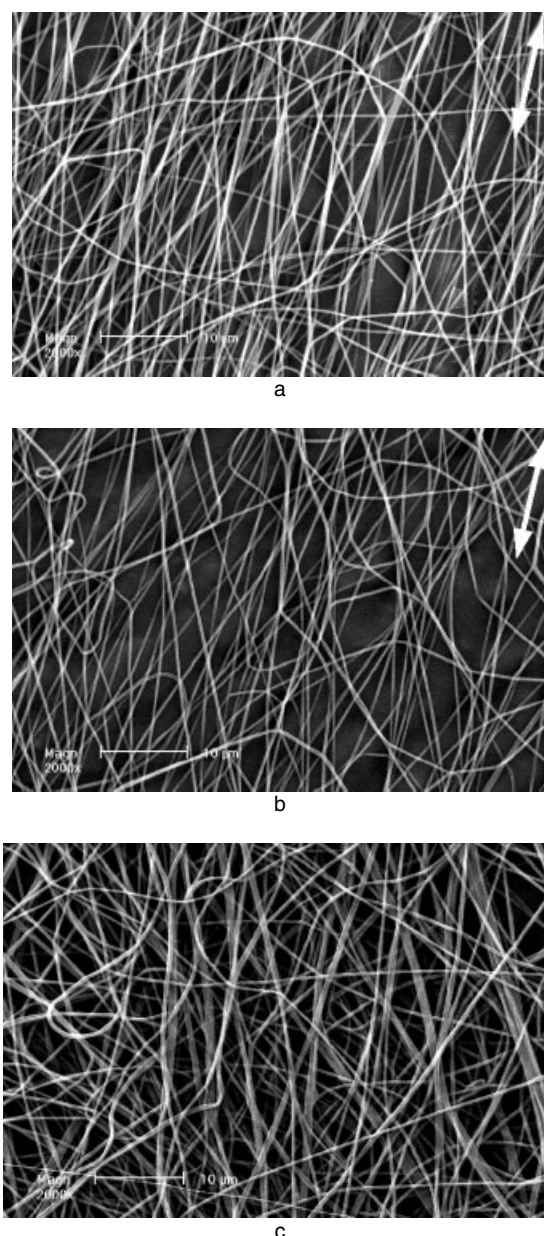


Figure 4. SEM micrographs of the ultrafine fibers electrospun from a 20 % PSF solution in DMAC/acetone (9:1) at (a) 10 kV, (b) 15 kV and (c) 20 kV. Arrows indicate the fiber arrangement direction. Flow rate = 0.66 ml h^{-1} , capillary–screen distance = 10 cm. (Original magnification: $2000\times$).

with various DMAC/acetone ratios at 10 kV with flow rate 0.66 ml h^{-1} and capillary–screen distance 10 cm are shown in Fig 3. From the pictures, bead-fiber morphology was obtained when 100 % DMAC was used as the solvent (Fig 3(a)), but beads in the picture have been deformed into long elliptical shapes drawn by the electrical force. The electrospun fibers in Fig 3(a) were conglutinated and distorted at their cross-points which could be clearly seen in the larger magnification picture ($10\,000\times$) shown in the lower right corner of Fig 3(a). The AFD in this case was $411 \pm 74\text{ nm}$ ($n = 10$).

When 10 % acetone was added to the polymer solutions, the bead morphology of the electrospun fibers almost disappeared (Fig 3(b)). There were no

beads in the pictures of the electrospun fibers when the acetone amount in the electrospun solutions increased to 20 % (Fig 3(c)) or 30 % (Fig 3(d)). Therefore, uniform ultrafine fibers formed when acetone was added to the solvent. The fibers were obviously smooth and their AFDs were 344 ± 51 nm ($n = 10$), 347 ± 24 nm ($n = 10$) and 294 ± 37 nm ($n = 7$) when DMAC to acetone ratios were 9:1, 8:2 and 7:3, respectively. The AFD values did not exhibit a significant difference ($P > 0.05$) between those obtained from solutions when the DMAC/acetone ratios were 9:1 and 8:2, but showed a significant decrease ($P < 0.05$) with an increase of the acetone amount in the solvent from 20 % to 30 %.

In addition to the increase in viscosity and surface tension of PSF solutions with the introduction of acetone, the higher volatility of acetone than DMAC could alter the electrospun fiber morphology and weaken the possibility of bead formation, even though the conductivity of the PSF solutions showed a sharp decrease. Therefore, the AFDs of the electrospun fibers exhibited a tendency to decrease from 100 % DMAC to 30 % acetone addition.

Applied voltage

SEM micrographs of the PSF fibers electrospun from a 20 % PSF solution in DMAC/acetone (9:1) at 10 kV, 15 kV and 20 kV are shown in Fig 4. Results suggested that uniform ultrafine fibers could be obtained in these high voltages when the flow rate was 0.66 ml h^{-1} and the capillary–screen distance was 10 cm. Additionally,

the ultrafine fibers obtained at 10 kV showed a clearly regular fiber arrangement, indicated by an arrow in Fig 4(a). This fiber arrangement was found along a circular direction on the collection screen forming a visible ‘white ring’. It could be considered a result of unstable whipping jets of the polymer solution. The image of the conical envelope of the instability zone has been photographed and analyzed by Reneker and Shin.^{3,6} The fiber arrangement at 15 kV became more irregular in Fig 4(b) because of more unstable moving of jets in the higher voltage electric field. The ultrafine fibers prepared at 20 kV (Fig 4(c)) almost lost their arrangement. Some ultrafine fibers in Fig 4(c) contacted each other because of the remaining electrostatic attraction between the fibers at the higher applied voltage.

The AFDs measured from SEM micrographs were 344 ± 51 nm ($n = 10$), 331 ± 26 nm ($n = 11$) and 323 ± 22 nm ($n = 11$) at 10 kV, 15 kV and 20 kV, respectively. The fiber diameter showed a slight tendency to decrease with the increase of the applied voltage, but they did not have significant differences among each other ($P > 0.05$).

Flow rate

Figure 5 shows that the SEM micrographs of the electrospun PSF fibers prepared at 0.40 and 0.66 ml h^{-1} flow rates from a 20 % PSF/DMAC solution at 10 kV voltage and 10 cm capillary–screen distance. The results indicated bead-fiber morphology when the flow rate was 0.66 ml h^{-1} (Figs 5(c) and (d)),

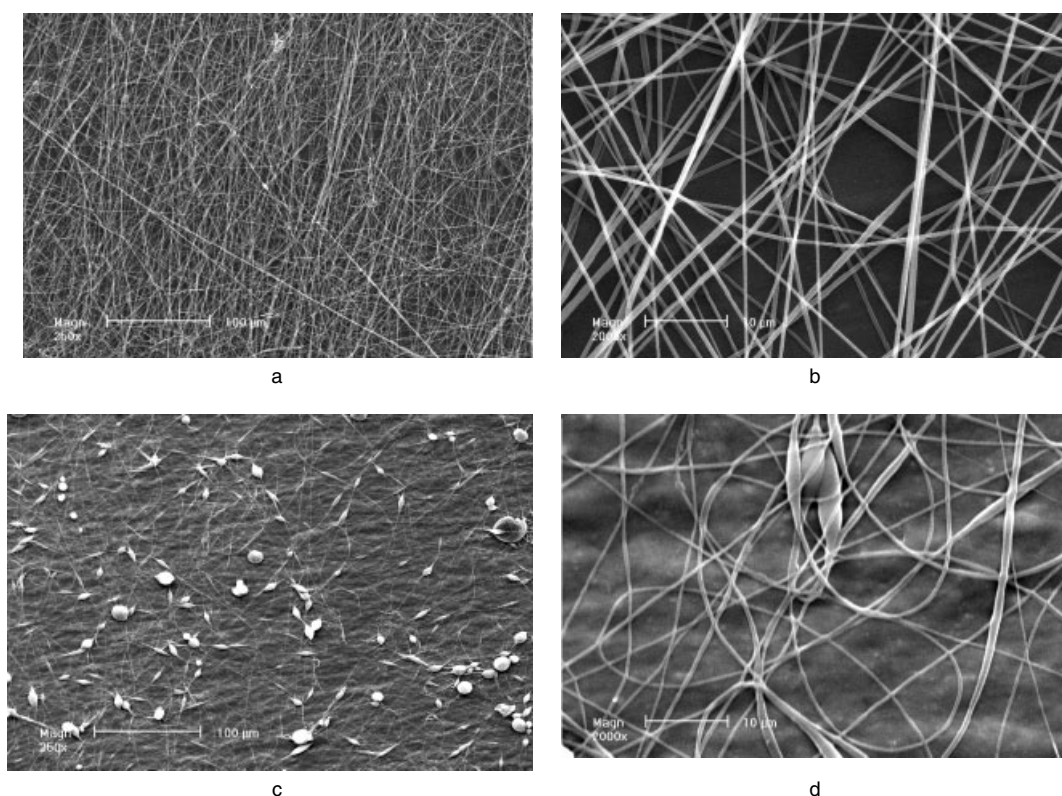


Figure 5. Effect of the flow rate on the morphology of the ultrafine PSF fibers electrospun from a 20 % PSF/DMAC solution at 10 kV. Flow rate = 0.40 ml h^{-1} (a, b) and 0.66 ml h^{-1} (c, d). Capillary–screen distance = 10 cm. (Original magnification a, c: 250 \times ; b, d: 2000 \times).

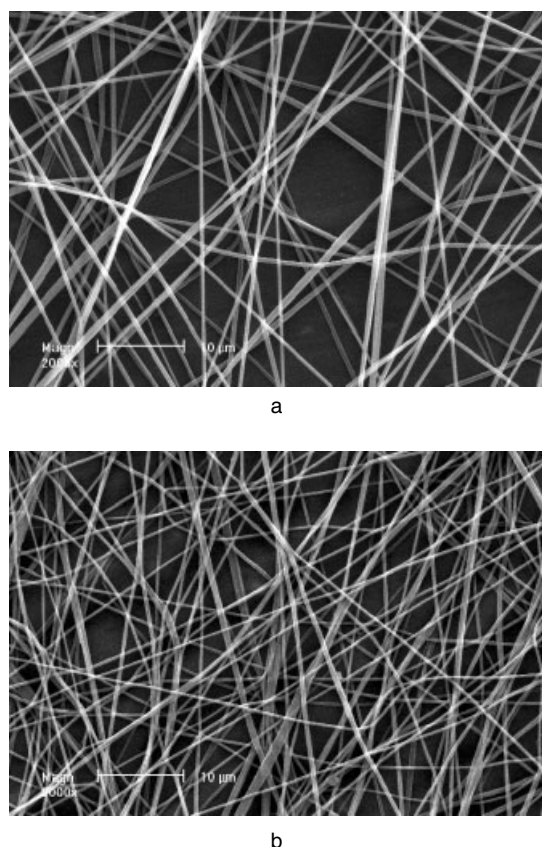


Figure 6. SEM micrographs of ultrafine PSF fibers prepared by electrospinning of a 20 % PSF/DMAC solution at 10 kV. Capillary–screen distance = (a) 10 cm and (b) 15 cm. Flowrate = 0.40 ml h^{-1} . (Original magnification: $2000\times$).

while uniform ultrafine fibers formed when the flow rate reduced to 0.40 ml h^{-1} (Figs 5(a) and (b)). The slower flow rate could have given the solvent much more time to evaporate so that the electrospun fibers could avoid bead formation.

Distance between capillary and collection screen

Figure 6 shows the SEM micrographs of the electrospun PSF fibers prepared at capillary–screen distances of 10 cm and 15 cm from a 20 % PSF/DMAC solution at 10 kV when the flow rate was 0.40 ml h^{-1} . It can be seen that there were no obvious differences between the morphologies of the electrospun PSF fibers at 10 cm and 15 cm, but the AFD of the electrospun fibers at 15 cm was $368 \pm 59 \text{ nm}$ ($n = 15$), significantly smaller ($P = 0.025$) than the AFD ($438 \pm 73 \text{ nm}$; $n = 11$) at 10 cm. Increasing the collection distance could give more time for the solvent to evaporate and for the charged fluids to split more times.

CONCLUSIONS

Ultrafine PSF fibers were prepared by electrospinning of PSF/DMAC or PSF/DMAC/acetone solutions. Results suggested that the solution concentration, acetone amount in the solution, the applied voltage, the flow rate and the capillary–screen distance

were the most important parameters influencing the morphology and the average diameter of the electrospun fibers. Increasing the polymer concentration and the acetone amount could produce uniform electrospun fibers rather than bead-fibers. Applying a lower flow rate was an alternative way to generate uniform electrospun fibers. Raising the applied voltage and increasing the capillary–screen distance tended to produce smaller diameters of the electrospun fibers. Typically, the uniform ultrafine PSF fibers with AFDs of about 300 to 400 nm could be prepared by electrospinning of the 20 % PSF solution in DMAC/acetone (9:1) at 10–20 kV high voltages and the 10 cm capillary–screen distance when the flow rate was 0.66 ml h^{-1} .

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