

Ultrafine Fibers Electrospun from Biodegradable Polymers

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ABSTRACT: Biodegradable poly(*l*-lactide) (PLLA) and poly(ϵ -caprolactone) (PCL) were electrospun into ultrafine fibers. The technological parameters influencing the spinning process and morphology of the fibers obtained were examined. These parameters included solvent composition, addition of certain organic salts, molecular weight and concentration of the polymers, capillary diameter, air ventilation, and pressure imposed on the surface of the solution as

well as electrostatic field. By properly choosing and adjusting these parameters, submicron PLLA and PCL fibers with a narrow diameter distribution were prepared. Scanning electronic microscopy was used to observe the morphology and diameter size of the fibers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1085–1092, 2003

Key words: biodegradable; fiber; polyesters; morphology

INTRODUCTION

Synthetic polymer fibers have been prepared for decades and are used in various applications such as textiles and resin reinforcement. Conventional techniques for forming polymer fibers include melt spinning,¹ wet spinning, and dry spinning. These techniques usually produce fibers with diameters in the range of 10–50 μm .²

In recent years there has been increasing interest in a novel process of fiber fabrication known as electrospinning, which can generate fibers with submicron diameters. Small fiber diameters and porous structures of the nonwoven mat of the electrospun fibers give rise to a large specific surface area.³ This is advantageous in a wide variety of applications, such as high-performance filters,^{4,5} scaffolds in tissue engineering,⁶ separation membranes,⁷ reinforcement in composite materials,⁸ templates for the preparation of functional nanotubes,⁹ and many others.^{10–12}

In the electrospinning process a strong electrostatic field is applied to a polymer solution held in a syringe with a capillary outlet. A pendant droplet of the polymer solution from the capillary outlet is deformed into a Taylor cone,¹³ or more precisely, a hyperbolic cone,¹⁴ by the electrostatic field. When the voltage surpasses a threshold value, the electric forces overcome the surface tension on the droplet, and a charged jet of the solution is ejected from the tip of the Taylor cone. As

the jet moves toward a collecting metal screen that acts as a counterelectrode, it is split into small charged fibers or fibrils,¹⁵ and the solvent evaporates. Thus, a nonwoven fabric mat is formed on the screen.

The behavior of electrically driven liquid jets has been of interest for many years, dating to the work of Rayleigh,¹⁶ who calculated the maximum amount of charge to be held on a drop of liquid before the electric field overcomes the surface tension of the drop. Taylor¹³ found that the cone with a semiangle of 49.3° from the capillary outlet formed under an electric field is stable. Yarin et al.¹⁴ recently analyzed the shape of the cone and found it to have a hyperbolic shape and a sharper critical angle. The first patent on polymer electrospinning was filed by Formals¹⁷ in 1934, but it did not draw enough interest because of the low efficiency of the technology. Baumgarten¹⁸ described the electrospinning of acrylic microfibers (500–1100 nm) in 1971. Larrondo and Manley studied the electrospinning of polyethylene and polypropylene melts.^{19–21} Reneker^{22,23} demonstrated electrospun DNA fibers and styrene–butadiene–styrene triblock copolymer fibers. Ultrafine conductive polyaniline fibers were electrospun by MacDiarmid.¹² Bognitzki prepared porous PLLA fibers via electrospinning and used them as a template (TUFT process) to prepare polymer, metal, and hybrid nano- or mesotubes.^{9,24} Theoretical studies were also conducted by Reneker, Baumgarten, and Shin et al.^{15,18,25} However, the efficiency and repeatability of electrospinning and the control of the fiber uniformity are still problematic; thus, the practical applications of electrospun fibers have been limited.

In this article we describe the electrospinning technique for the preparation of ultrafine and uniform PLLA and PCL fibers. PLLA and PCL are well-known

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biodegradable polymers, but their biodegradation rate is quite slow for some biomedical applications such as tissue engineering. Among the efforts to speed up the biodegradation rate of PLLA and PCL, increasing their surface area by processing them into ultrafine fibers and nanoparticles is an effective way.²⁶ Therefore, we examined the influences of the spinning parameters, such as solvent composition, addition of certain organic salts, molecular weight and concentration of the polymers, capillary diameter, air ventilation and pressure imposed on the surface of the solution as well as the electrostatic field. By properly choosing and adjusting these parameters, submicron PLLA and PCL fibers with a narrow diameter distribution were prepared.

EXPERIMENTAL

Poly-*l*-lactide (PLLA) and poly(ϵ -caprolactone) (PCL) were synthesized in xylene using 0.1 wt% stannous octoate catalyst, which was carried out at 120°C for 24 h. The intrinsic viscosity $[\eta]$ of the polymers was measured in benzene at 30°C using an Ostwald viscometer, and the viscosity-average molecular weight (M_v) was calculated by the following formulas:

$$\begin{aligned} [\eta] &= 9.94 \times 10^{-5} M_v^{0.82} \text{ for PCL}^{27} \\ [\eta] &= 5.45 \times 10^{-4} M_v^{0.73} \text{ for PLLA}^{28} \end{aligned} \quad (1)$$

The solvent systems used in the electrospinning experiments included chloroform, chloroform–acetone, 1,2-dichloroethane, and chloroform–1,2-dichloroethane. PLLA and PCL solutions with different concentrations were prepared and gently stirred for 24 h at room temperature in order to obtain a homogenous solution. Triethyl benzyl ammonium chloride (TEBAC) was added into the solution to improve the continuity of spinning.

The apparatus used for electrospinning is shown in Figure 1. The solution was added in a 5-mL syringe, which had attached to it a right-angle-shaped metal capillary with an inner diameter of less than 0.5 mm. A high voltage (from a GF-II-type generator, voltage range 0–80 kV, limiting current 50 μ A) was applied to the metal needle. A circular-shaped counterelectrode was about 20 cm from the capillary tip. Pressure was applied to the solution in a syringe by putting a certain weight on the top of the piston to maintain a steady flow of the solution from the capillary outlet.

The morphology of the electrospun fibers was observed with a scanning electron microscope (SEM; JXA-840 from JEOL), and the accelerating voltage was 20 kV.

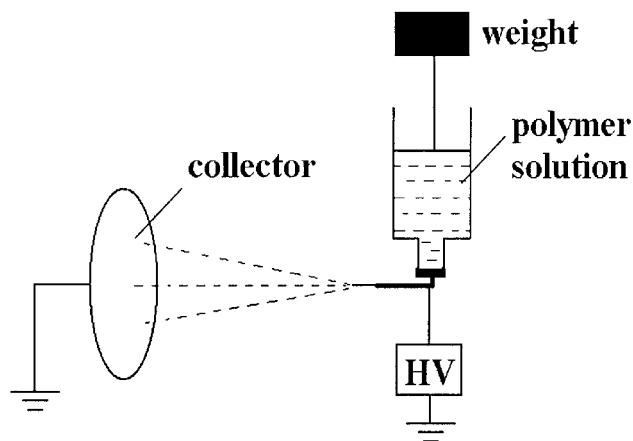


Figure 1 The apparatus used for electrospinning.

RESULTS AND DISCUSSION

Effect of solvent

In the electrospinning experiments solvent had a significant influence on the morphology and diameter size of the electrospun fibers. Raimund Jaeger et al.²⁹ electrospun fibers from PEO–water solutions and observed a beads-on-a-string morphology. Fong et al.³⁰ discussed comprehensively the beads observed during electrospinning. Bognitzki et al.²⁴ used dichloromethane as solvent and prepared PLLA fibers with a regular pore structure. In our experiments the PLLA fibers prepared from a chloroform solution had a rough and porous surface, and their diameters ranged from 500 nm to 3 μ m. While using a mixed solvent of chloroform and acetone with a 3:1 volume ratio, the morphology of the fibers was significantly improved—that is, the surface of the fibers became smooth and the diameter size uniform. When the volume ratio was changed to 1:1, the diameter of the fibers became very uniform and much smaller, to about 600 nm. The SEM micrographs of the fibers are shown in Figure 2.

It was observed that the length of the jet from the tip of the capillary to the point of splaying was related to the acetone content in the solution. When chloroform acted as the single solvent, the length of the jet was about 10–15 cm, compared to 5–8 cm of the jet length for PLLA/chloroform–acetone (3:1) solution and 2–3 cm for PLLA/chloroform–acetone (1:1) solution. Moreover, the addition of acetone to the solution led to improved continuity of the process. But when using acetone as the single solvent, the blockage of the capillary tip occurred frequently because of its rapid evaporation. The relationship between jet length and solution composition is shown in Table I.

Our interpretation of these results is that acetone has smaller polarity than chloroform and thus combines with the polymer molecules more loosely. Consequently, the jet has less cohesive energy and can

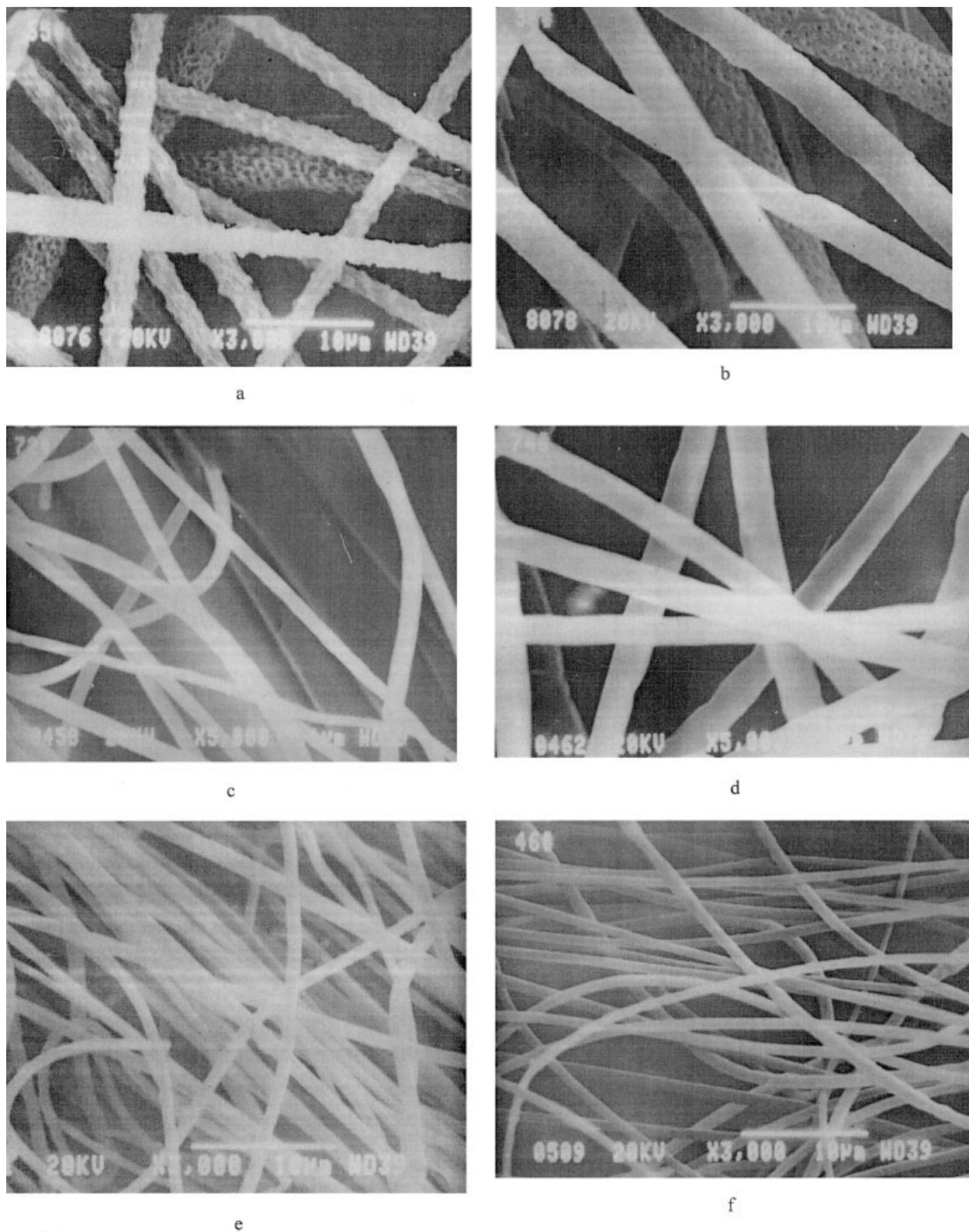


Figure 2 SEM micrographs of electrospun fibers: (a) 6.4% PLLA/chloroform; (b) 6.6% PLLA/chloroform; (c) 7.4% PLLA/chloroform-acetone (3:1); (d) 8% PLLA/chloroform-acetone (3:1); (e) 9.3% PLLA/chloroform-acetone (1:1); (f) 8.5% PLLA/chloroform-acetone (1:1). M_w of PLLA = 48,000.

TABLE I
The Relation Between Jet Length and Solution Composition*

Solvent systems	Chloroform	chloroform-acetone (3:1)	chloroform-acetone (1:1)	1,2-dichloroethane	chloroform-1,2-dichloroethane (1:1)	chloroform-acetone (1:1)-5% TEBAC	1,2-dichloroethane-5% TEBAC	chloroform-1,2-dichloroethane (1:1)-5% TEBAC
Concentration (wt %)	3.8-6.0	6.8-8.0	7.0-8.5	7.3-8.0	4.5-7.5	6.5-8.5	7.3-8.0	4.5-7.5
Driving voltage (kV)	22	15	25	1.8	20	35-40	40	40
Jet length (cm)	10-15	5-8	2-3	5-8	—	0.5-1	0.5-1	1

* The experimental material is PLLA. Its M_v is 48,000. The ratios in parentheses are volume ratios. The capillary outlet diameter is 0.5 mm.

splay more easily, resulting in a shorter jet length and more uniform fiber diameter.

Effect of organic salt

A significant decrease in diameter and more uniform distribution of fiber diameters were achieved by add-

ing a small amount of triethyl benzyl ammonium chloride (TEBAC) into the polymer solution. As shown in Figure 3, the fibers prepared from 8% PLLA ($M_v = 48,000$)/1,2-dichloroethane solution had diameters from 450 nm to 1.6 μm , while those from the same solution containing 5% TEBAC had a diameter of about 500 nm. The related data are listed in Table I.

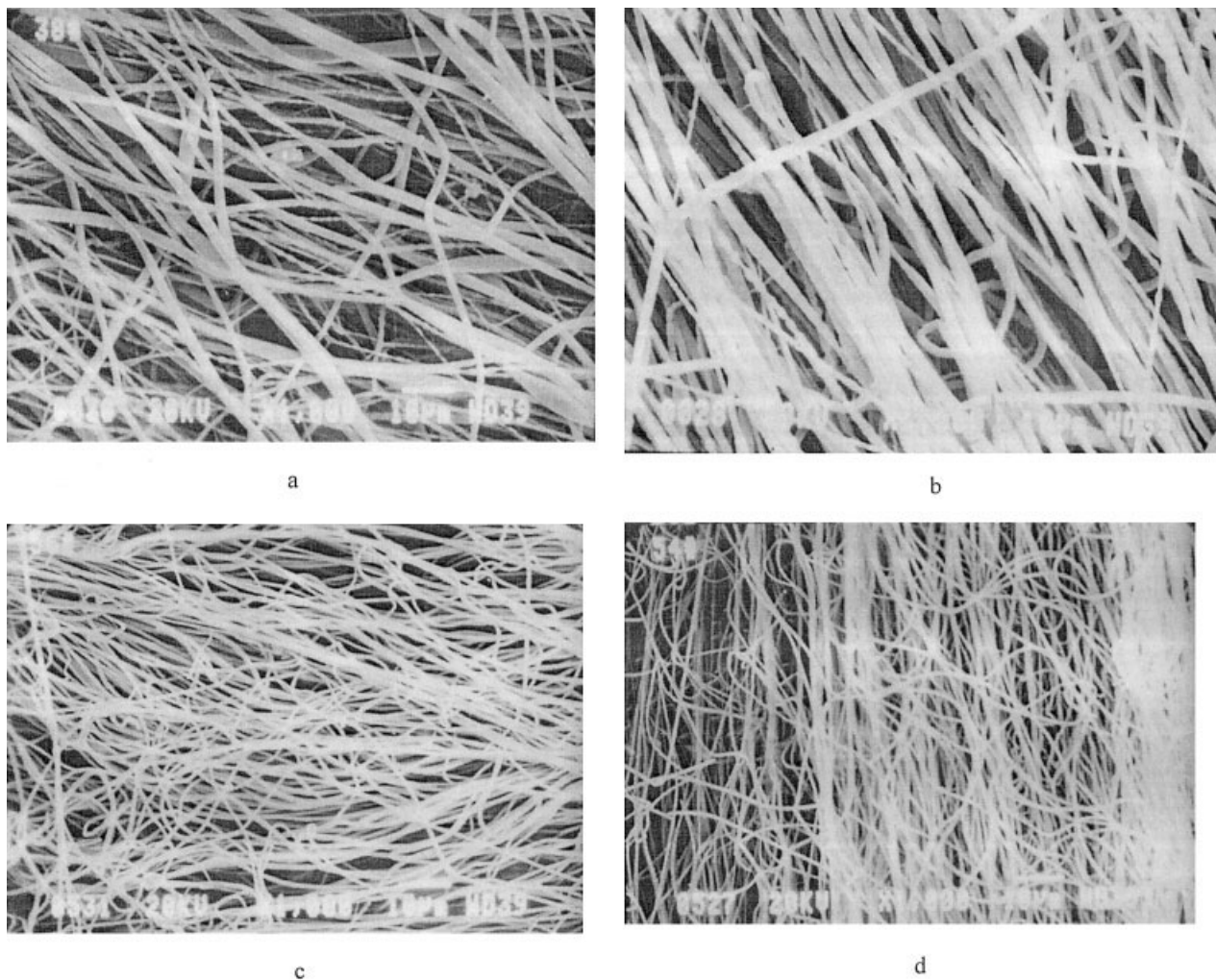


Figure 3 SEM micrographs of electrospun fibers: (a) 7.3% PLLA/1,2-dichloroethane; (b) 8% PLLA/1,2-dichloroethane; (c) 7.3% PLLA/1,2-dichloroethane-5% TEBAC; (d) 8% PLLA/1,2-dichloroethane-5% TEBAC. M_v of PLLA = 48,000.

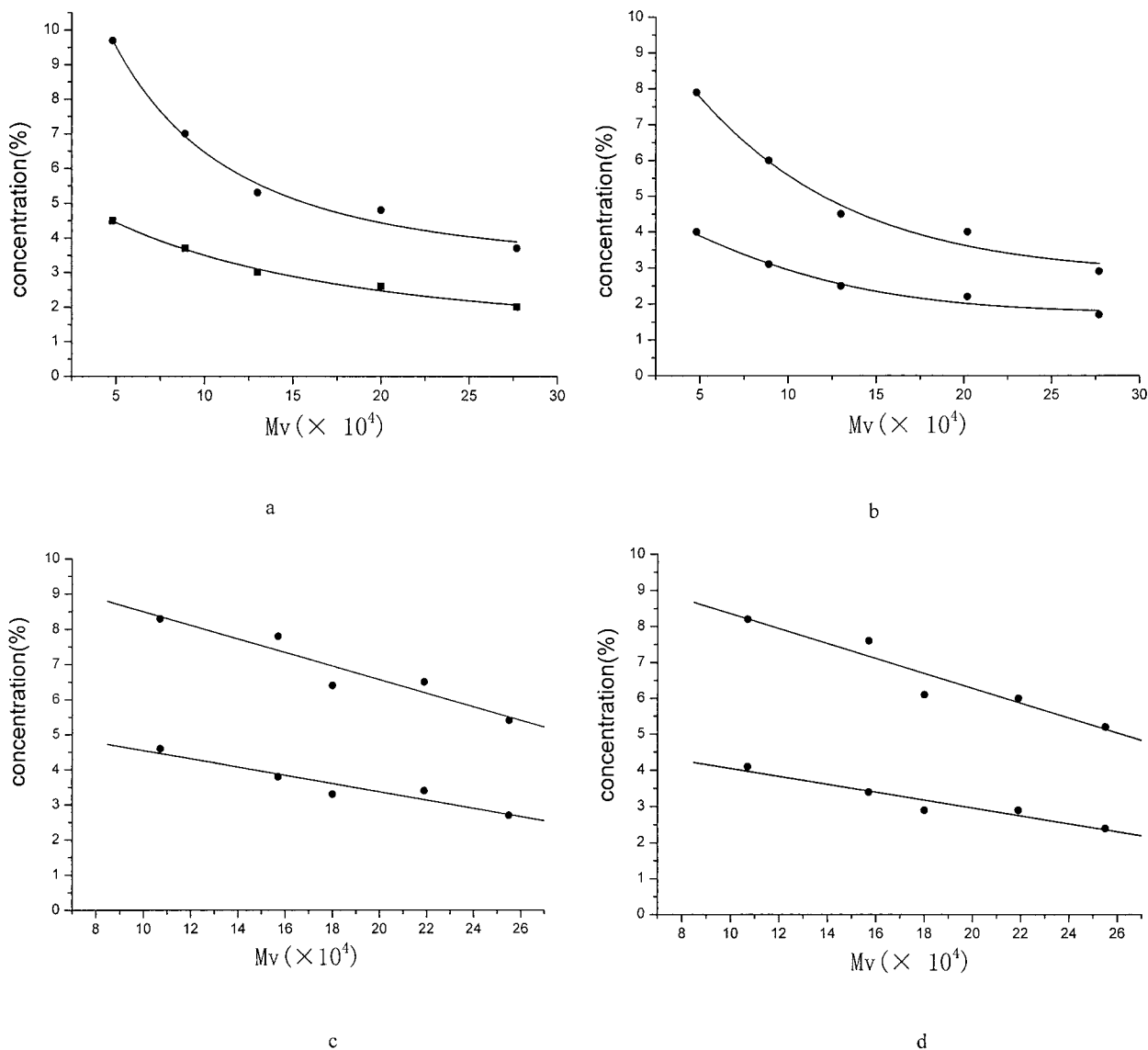


Figure 4 Electrospinnable concentration range of PLLA and PCL: (a) PLLA/chloroform-acetone (1:1); (b) PLLA/chloroform-1,2-dichloroethane (1:1); (c) PCL/chloroform-acetone (1:1); (d) PCL/chloroform-1,2-dichloroethane (1:1).

This improvement may be attributed to the shortened jet length (Table I) and easier splitting of the jet caused by the addition of TEAC.

We also examined other organic salts such as sodium dodecyl benzene sulfonate and sodium dodecyl sulfate. No significant improvement in the electrospinning process and the fiber morphology was observed.

Spinnable concentration range and its molecular weight dependence

A spinnable concentration range was observed for a polymer with a given molecular weight; outside this range either the electrospinning was impossible, or many beads appeared on the fibers obtained. Figure 4 shows this concentration range (between the two curves) as a function of molecular weight of the polymer. With increasing molecular weight, the spinnable

concentration range narrowed. This means electrostatic spinning will be more difficult to control if the molecular weight is very high. It also can be seen (Fig. 4) that the two solvent systems examined did not make an appreciable difference for a given polymer, whereas PCL showed a wider spinnable concentration range than PLLA in both.

It is well known that molecular weight has a significant influence on solution viscosity. As for apparent viscosity, a higher molecular weight was equivalent to a higher concentration. Therefore, for a polymer with a given molecular weight, a proper concentration within its spinnable concentration range should be first chosen. Generally speaking, the higher its molecular weight, the less concentrated the solution should be. In this way fibers with a uniform diameter size and smooth surface could be obtained for polymer sam-

ples with different molecular weights, as shown in Figure 5.

Driving voltage and its solution composition dependence

According to the principle of electrospinning, a strong enough electric field (starting voltage) is needed to overcome the surface tension on a liquid droplet and thus to realize jet ejection from the Taylor cone. Actually, the voltage should be adjusted to a proper value to maintain a continuous and steady spinning. This is termed "driving voltage." It is dependent on solution composition. As shown in Table I, a much higher voltage is needed for solutions containing TEBAC. This is likely to be a result of the possible polarization and ionization of TEBAC under the electrostatic field. Because the induced field possesses an opposite direction to the external field, a higher driving field is needed.

Effect of pressure

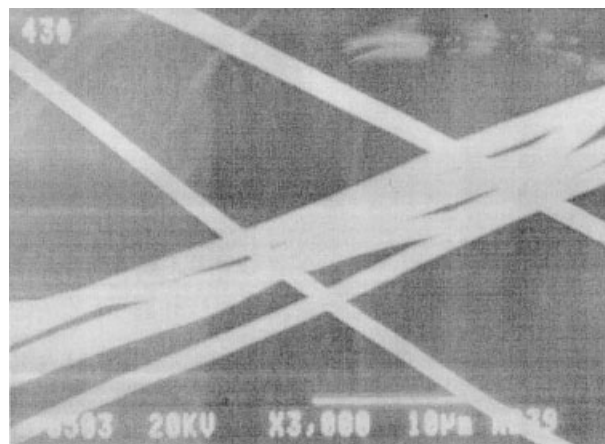
To maintain a continuous and steady spinning and to raise the productivity of electrospinning, pressure was applied to the solution in the syringe, as shown in Figure 1. This pressure speeded up the flow rate of the solution through the capillary and thus influenced the whole spinning process, especially affecting the relative rate of solvent evaporation compared to jet flow. In extreme case, when the pressure was too high, the fiber mat obtained on the collecting screen was wet and adhesive—there was residual solvent in it. The fiber diameters looked less uniform, as shown in Figure 6.

Effect of capillary outlet diameter

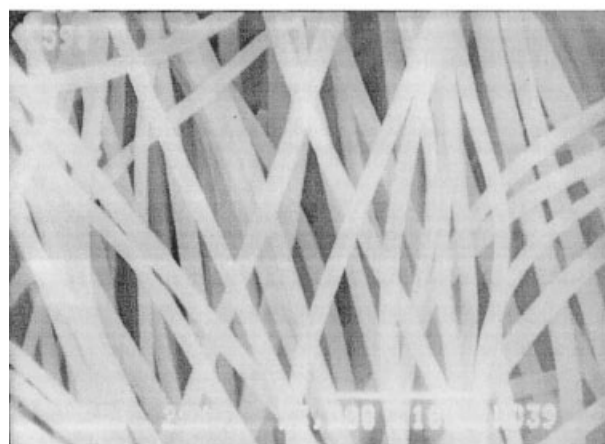
The influence of the capillary outlet diameter was examined experimentally. When different outlet diameters are employed, the driving voltage should be properly adjusted in order to achieve successful spinning. For example, when the outlet diameter was 0.1 mm, the driving voltage was about 29 kV, whereas when the outlet diameter was 0.4 mm, the driving voltage should have been raised to about 36 kV. This might be because of the increased flow rate from the wider outlet. Correspondingly, different fiber diameters were obtained, as shown in Table II.

Effect of ambient temperature and air flow

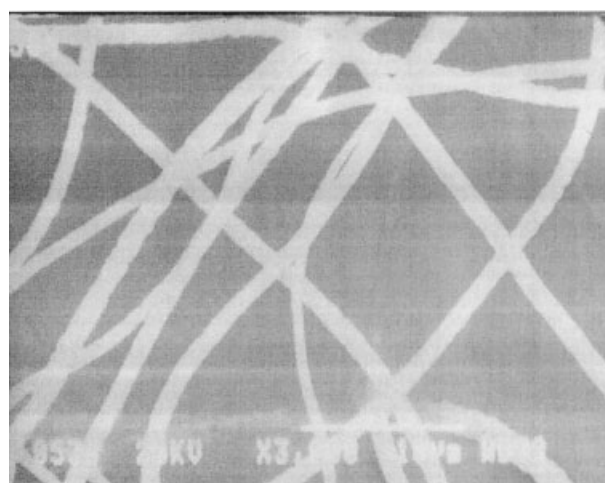
Solvent evaporation is one of the key steps in electrospinning, and thus ambient temperature is a very important factor. Our experience is that electrospinning is often successful in summer but difficult in winter. Figure 7(a) shows the electrospun fibers pre-



a

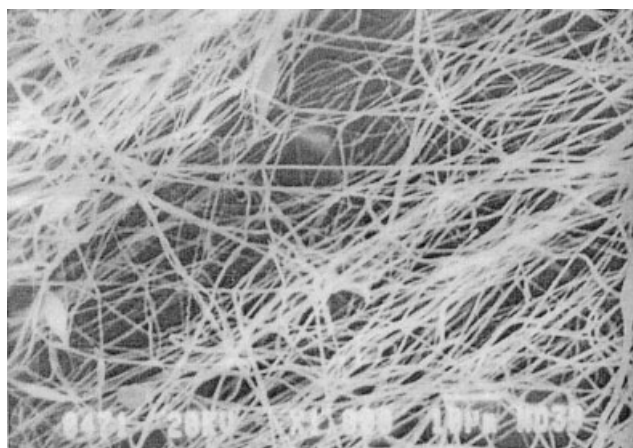


b

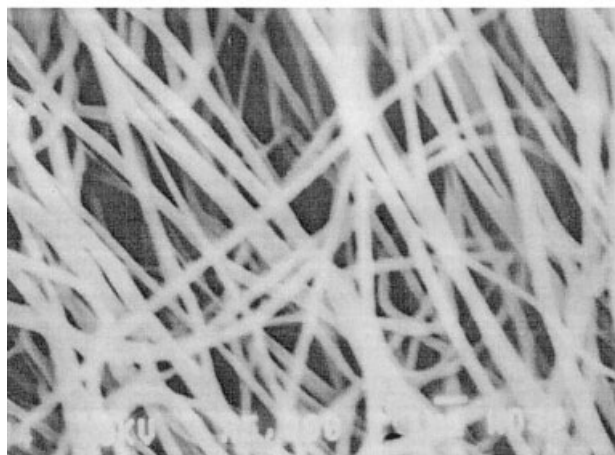


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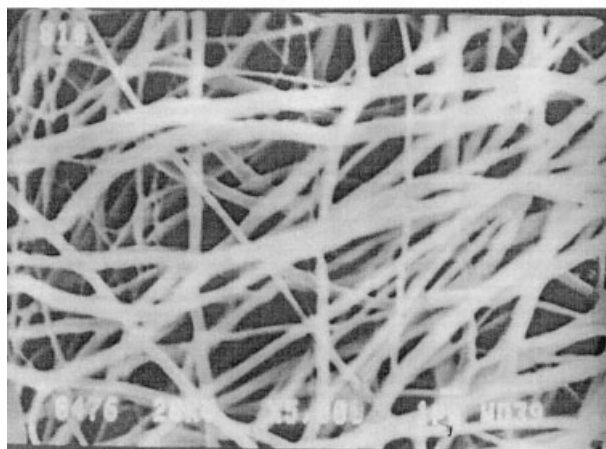
Figure 5 SEM micrographs of fibers from PLLA/chloroform-acetone (1:1) solutions in which PLLA has different molecular weights: (a) concentration is 9.1%, $M_n = 48,000$; (b) concentration is 4.1%, $M_n = 200,000$; (c) concentration is 3.7%, $M_n = 270,000$.



a



b



c

Figure 6 SEM micrographs of fibers from 5.4% PLLA/chloroform–acetone (1:1) under different pressures (flow rates): (a) 5000 Pa, 0.03 mL/min; (b) 10,000 Pa, 0.05 mL/min; (c) 15,000 Pa, 0.1 mL/min. M_v of PLLA = 48,000.

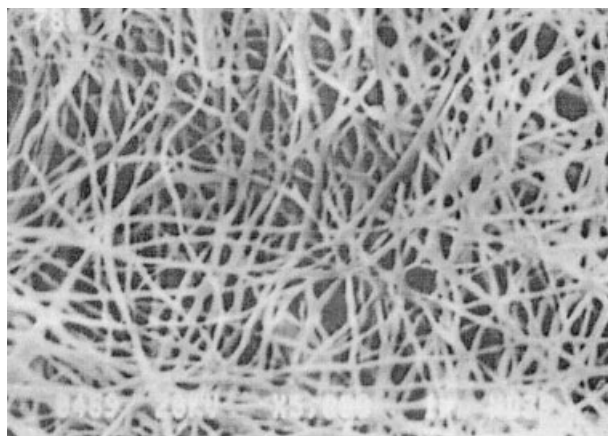
pared at room temperature (25°C) in summer. They looked straight, and their diameters were uniform. When the same spinning conditions were adapted in

TABLE II
Effect of Capillary Inner Diameter on Electrospinning Process and Fiber Diameter*

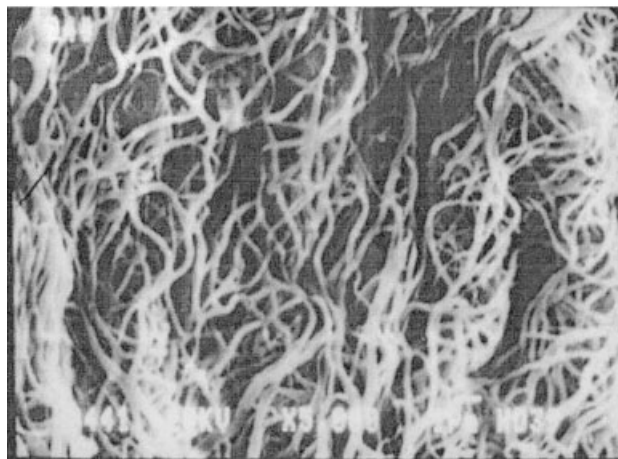
Capillary diameter (mm)	Driving voltage (kV)	Fiber diameter (nm)
0.1	29	300–400
0.2	30	400–500
0.4	36	900

* The experimental solution is 4.5% PCL/chloroform-1,2-dichloroethane (1:1)–5% TEAC. The M_v of PCL is 480,000.

winter at room temperature (7°C), the spinning was not satisfactory because of the slower evaporation rate. Therefore, the spinning apparatus was housed in a cabinet, and a heater was put inside to warm up the temperature to about 25°C. Consequently, the fibers shown in Figure 7(b) were obtained. Obviously, they were badly coiled and entangled. This morphology



a



b

Figure 7 SEM micrographs of fibers from 2.5% PLLA/chloroform-1,2-dichloroethane (1:1) solution–5% TEAC: (a) at 25°C (room temperature); (b) heated to 25°C in experimental space (although room temperature was 7°C). M_v of PLLA = 130,000.

may be attributed to the air circulation in the cabinet caused by heating.

CONCLUSIONS

Ultrafine fibers were electrospun from biodegradable PCL and PLLA. The influences of the technological parameters on the spinning process and the morphology of the fibers obtained were examined systematically. These parameters include (1) solution composition, such as mixed solvent and inclusion of organic ammonium salt; (2) spinnable concentration or viscosity range of the solution, which is dependent on solution composition and molecular weight of the polymer; (3) capillary outlet diameter; (4) pressure in the solution; (5) driving voltage, which depends on the above parameters; and (6) ambient temperature and air flow near the spinning apparatus. By properly choosing and adjusting these parameters, submicron fibers with uniform diameters and smooth surfaces were obtained. The criteria for the parameter adjustment were formation of the Taylor cone, jet ejection from the Taylor cone, length and stability of the solution jet, splaying of the jet, shape, diameter size and distribution of the fibers obtained, and solvent content in the fibers.

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