Preparation of Core/Shell PVP/PLA Ultrafine Fibers by Coaxial Electrospinning

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ABSTRACT: This study investigated the process feasibility and stability of core/shell structured bicomponent ultrafine fibers of poly(vinyl pyrrolidone) (PVP) and poly(D,L-lactide) (PLA) by coaxial electrospinning. The morphological structure of the core/shell ultrafine fibers was studied by means of scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. Results suggested that PVP/PLA core/shell ultrafine fibers with drawbacks could be produced from 6 or 8% PVP solutions (inner) in the mixture of *N*,*N*-dimethlformamide (DMF) and ethanol and a 22% PLA solution (outer) in DMF and acetone when the flow rates of inner and outer fluids were 0.05 and 0.1 mL/h, respectively. The tensile modulus and tensile strength of the core/shell PVP/PLA membrane were dramatically lower than those of the electrospun PLA membrane, and its water uptake was twice more than that of the PLA membrane. Membranes made from the biodegradable core/shell ultrafine fibers could be potentially used in loading bioactive molecules for tissue regeneration. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 39–45, 2006

Key words: coaxial electrospinning; core/shell; ultrafine fiber; poly(D,L-lactide); poly(vinyl pyrrolidone)

INTRODUCTION

Owing to a high voltage electric field between a metal capillary containing a polymer solution and a ground collector, electrospinning is a unique process by which ultrafine fibers with diameter ranging from nanometers to micrometers can be prepared.[1,2] Ultrafine polymeric fibers prepared by electrospinning could be potentially applied in many areas such as tissue engineering scaffolds,[3–5] carriers of drugs or enzymes,[6,7] sensors,[8,9] etc. Since core/shell structures could enhance material properties for the above applications, the core/shell fibers have gained much attention recently. In biomedical areas, such core/shell nanostructures could preserve an unstable biological agent from aggressive environments, deliver a biomolecular drug in a sustained way, and functionalize the surface of nanostructures without affecting the core material. Also, with the core/shell structure, ultrafine fibers could also load two different kinds of bioactive molecules or drugs in the core and the shell, respectively, and thus they could be released in a controlled manner for different times for different aims. There are several methods for preparing core/shell fibers: the TUFT (tubes by fiber templates) process,[10] self-assembly,[11] template synthesis,[12] and the recently developed coaxial electrospinning.[13–17] Among them, coaxial electrospinning was expected to be the simplest and the most efficient technique.

Locertales et al. initially demonstrated that the coaxial spinneret could be used to prepare the core/shell jet.[18] However, the experimental instability resulted in breakup of the core/shell jet and formation of nanoparticles. They also studied the effect of system and process parameters on coaxial electrospinning, including viscosity, electrical conductivity and surface tension of electrospun polymer solutions, the applied voltage, and the fluid flow rates.[19] The core/shell ultrafine fibers were produced successfully by Sun and his coworkers.[13] Three kinds of core/shell fibers, made of two identical polymers, two different polymers, and polymer/metal oxide, were prepared in their experiments. Yu et al.[14] investigated the appropriate electrospun conditions of several polymer systems, including polyacrylonitrile/poly(acrylonitrile-*co*-styrene), poly(aniline sulfonic acid)/poly(vinyl alcohol), and *Bombyx mori* silk/poly(ethylene oxide). Results suggested that the miscibility of the two solutions could reduce the interfacial tension between the inner and outer fluid streams, and thus ultrafine fibers with even smaller diameters could be produced. However, Li and Xia[15] considered the immiscibility of core and sheath liquids to be most crucial to the formation of uniform core/shell or hollow fibers. Huang and coworkers[16] demonstrated that the shell thickness could be controlled by varying the concentration of the inner solution. Increasing the inner polymer concentration also resulted in an increase in both core and

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whole sizes. Ramakrishna and his coworkers prepared collagen-coated poly(ε-caprolactone) ultrafine fibers in the core/shell structure by the coaxial electrospinning technique and indicated that the core/shell composite fibers could improve proliferation of human dermal fibroblasts.[17]

In this study, core/shell structured bicomponent ultrafine fibers were prepared from poly(D,L-lactide) (PLA) and poly(vinyl pyrrolidone) (PVP) to look for a new way in loading bioactive molecules for applications in tissue regeneration.

MATERIALS AND METHODS

Materials

PVP with a weight-average molecular weight of 1.3 $\times$ 10^6 was purchased from Alfa Aesar, USA. Amorphous PLA was supplied by the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, China. The intrinsic viscosity (η) of PLA was 1.43 dL/g.

Preparation and properties of the electrospun solutions

PVP solutions with 4–10% concentrations were prepared by dissolving the powdered polymer in the mixture of *N*,*N*-dimethlformamide (DMF) and ethanol (50 : 50, w/w). PLA was dissolved at a concentration of 22% in the mixture of DMF and acetone (80 : 20, v/v). The polymer concentration was designated to the percentage of polymer mass (g) in solvent volume (mL). The surface tension of each solution was measured at room temperature by the Wilhelmy plate method with a tensiometer (DCAT21, Dataphysics, Germany), while the clean platinum plate was used. The solution viscosity was determined by using a rotating viscometer (Model NDJ-79, Shanghai, China) at 25°C. The conductivity of polymer solutions was determined in a conductivity instrument (Model DDS-11A, Shanghai, China).

Coaxial electrospinning

The schematic setup of coaxial electrospinning in this study is shown in Figure 1. It was essentially the same as that of a conventional electrospinning setup in our previous report,[20] except for replacing the single capillary with a coaxial spinneret consisting of two concentrically arranged capillaries that were flatted stainless steel needles. A certain amount of the two polymer solutions were contained separately in two medical syringes connected to the coaxial spinneret, respectively. The flow rate in each capillary was adjusted in a double-way syringe pump. The inner capillary had an inner diameter (ID) of 0.37 mm and an outer diameter (OD) of 0.70 mm, while the outer capillary had an ID of 0.80 mm and an OD of 1.20 mm. Both capillaries were connected to the same electrical potential, provided by a high voltage power supply (GDW-A, Tianjin University, China). A piece of grounded aluminum foil was placed below the capillary tip as the collector. The electrospun fibers were typically obtained at 6 kV and 15 cm capillary–collector distance. The electrospun nonwoven membranes were dried in a vacuum oven at room temperature for 12 h to remove the residual organic solvent before characterization.

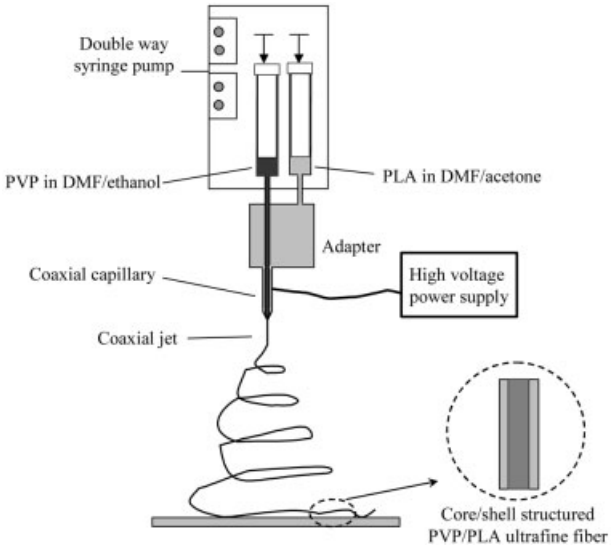

Figure 1 Schematic setup of coaxial electrospinning.

Characterization

The morphology of the electrospun fibers of PVP/PLA was observed under a scanning electron microscope (SEM, Philips XL-30) after gold coating. The average fiber diameter of the electrospun fibers was measured by Adobe Photoshop 7.0 software from the SEM micrographs at 10K$\times$ magnification. Verification of the core/shell structure of electrospun fibers was conducted using a JEOL JEM-100CX II transmission electron microscope (TEM) operated at 100 keV. The samples for the TEM observation were prepared by directly depositing the as-spun fibers onto the copper mesh coated with carbonic film. Analysis of X-ray photoelectron spectroscopy (XPS) was carried out on a PerkinElmer PHI-1600 spectrometer using Mg Kα radiation (1253.6 eV, 250 W).

Mechanical properties of electrospun membranes of PVP/PLA as well as PLA were tested in a universal testing machine (Testmetric M350–20KN, UK) equipped with a 100 N load-cell. Samples were cut into 60 $\times$10 mm^2 and the gauge length was 40 mm. Each tensile test was operated under a crosshead

speed of 5 mm/min at room temperature. The reported tensile modulus, tensile strength, and elongation represent the average results of five tests.

Three pieces of electrospun PLA and PVP/PLA membranes, which were cut into a square shape with dimensions of 20 × 20 mm^2, were accurately weighed in an electronic balance and placed into glass bottles. Phosphate-buffered saline (PBS; 20 mL, pH = 7.40) was added in each bottle. The samples were incubated in PBS at (37.0 ± 0.1)°C for 24 h and then weighed again immediately after removing them from PBS and absorbing surface water with a filter paper. The water uptake of the electrospun membranes were calculated using the following equation:

$$\text{Water uptake} = (m_1 - m_0)/m_0 \times 100\% \qquad (1)$$

where m_0 and m_1 are the masses of the membranes before and after immersion in the medium, respectively.

RESULTS AND DISCUSSION

Because of good biodegradability and processibility, PLA and its copolymers with glycolide or ε-caprolactone have been used in biomedical applications for many years. PVP is a water-soluble polymer and has been widely used as an additive for medicines. Core/shell ultrafine fibers of these two polymers were prepared by coaxial electrospinning in this work and it is suggested that the ability of loading bioactive molecules would be enhanced for their applications in tissue engineering scaffolds.

First, aqueous PVP solutions were tested in the formation of core/shell ultrafine fibers with PLA solution in DMF/acetone. Unfortunately, this coaxial electrospinning process was stopped by agglomeration of PLA at the capillary tip. Therefore, a mixed solvent of DMF and ethanol was used instead of water for dissolving PVP. A series of PVP solutions with concentrations of 4–10% were examined. Effects of system parameters, including the PVP concentration and the solution flow rates, on the morphological structure of the core/shell fibers were investigated.

TABLE I
Properties of the PVP Solutions for Coaxial Electrospinning with PLA

Concentration (%)	Surface tension (mN/m)	Viscosity (cP)	Conductivity (μS/cm)
4	27.44	14	24
6	27.47	30	29
8	27.97	64	28
10	28.12	93	31

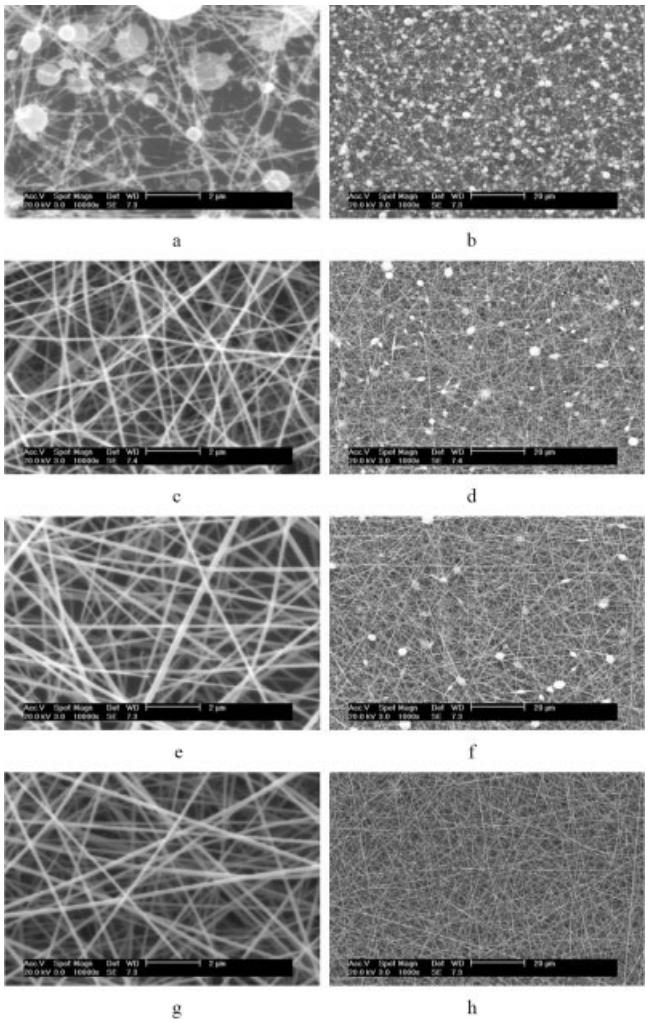

Figure 2 SEM micrographs of electrospun fibers from PVP solutions at different concentrations: (a,b) 4%; (c,d) 6%; (e,f) 8%; (g,h) 10% (a,c,e,g: ×10K; b,d,f,g: ×1000).

PVP concentration

The properties of PVP solutions in DMF/ethanol (1/1 in volume) with different concentrations are shown in Table I. The surface tension changed slightly as the concentration was increased, ranging from 27.44 mN/m (4%) to 28.12 mN/m (10%), whereas the viscosity of the PVP solutions increased significantly from 14 cP (4%) to 93 cP (10%). The solution conductivity had a tendency to increase but ranged from 28 to 31 μS/cm when the PVP concentration was in the range from 6 to 10%. To investigate the effect of PVP concentration, PVP solutions were electrospun in the general single-fluid mode before coaxial electrospinning. Figure 2 shows the SEM micrographs of the electrospun PVP membranes. At 4% concentration, the solution was too dilute to form continuous jets and heavily beaded fibers were formed instead [Figs. 2(a) and 2(b)]. The increase of the concentration of PVP solution resulted in formation of ultrafine fibers with

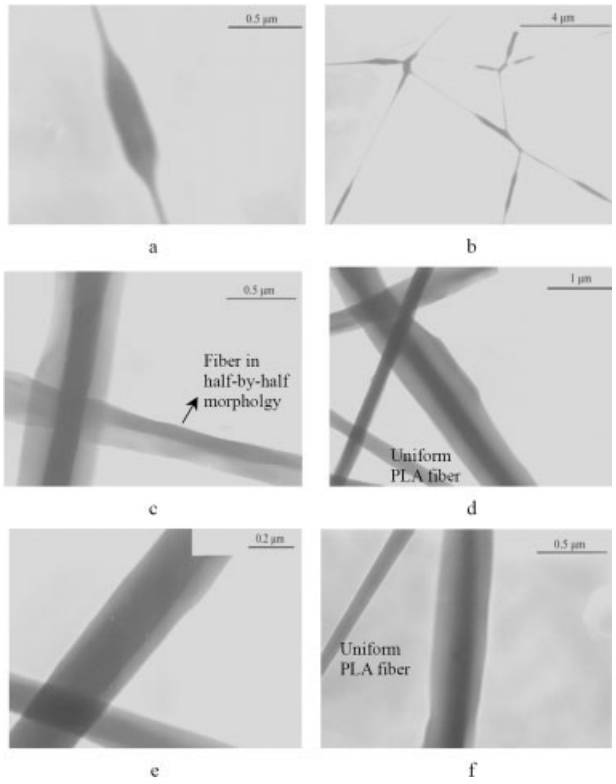

Figure 3 TEM micrographs of electrospun PVP/PLA obtained from a 22% PLA solution and PVP solutions at different concentrations: (a,b) 4%; (c,d) 6%; (e) 8%; (f) 10% (a,e,f: ×36K; b: ×5800; c: ×58K; d: ×19K).

less beads, as shown in Figure 2(c,f). The average diameter of the fibers electrospun from 6 or 8% PVP solutions was 114 ± 28 and 148 ± 32 nm, respectively. When the concentration reached to 10%, the beads disappeared while the average fiber diameter was 170 ± 26 nm [Fig. 2(g,h)].

Figure 3 shows the TEM micrographs of the coaxial electrospun membranes from PVP solution at different concentrations as the inner solution and a 22% PLA solution as the outer solution while process variables were held constant. The core/shell structure appearing in TEM micrographs could be attributed to the presence of nitrogen in PVP, which enhanced the contrast over that of PLA. The coaxial electropun ultrafine fibers prepared by the 4% PVP solution and the 22% PLA solution were not in the core/shell structure because of the low viscosity of the PVP solutions and the instability of electrospinning. The composite PVP/PLA fibers from 4% PVP appeared to have the beads-on-strings morphology [Fig. 3(a,b)]. Fine electrospun PVP/PLA core/shell fibers were prepared when the viscosity of PVP solutions increased to 30 cP or higher. At concentration of 6% or higher of PVP solutions, core/shell structured ultrafine fibers with rough surface were prepared [Fig. 3(c–f)]. The TEM micrographs also indicate that the composite ultrafine fibers were not perfect in cylindrical morphology but exhibited half-by-half core/shell [Fig. 3(c)] or uniform PLA, as shown in Figure 3(d,f). The core/shell fibers had a diameter about 500 nm, with a core diameter between 200 and 300 nm. When the PVP concentration reached to 10%, the core/shell fibers could also be observed [Fig. 3(f)], though the coaxial electrospinning process could not perform facilely due to the higher viscosity of the PVP solution.

The SEM micrographs show the diameter distributions of core/shell fibers (Fig. 4). These fibers were both core/shell structured from Figure 3. The average diameter of the fibers prepared from different concentrations of PVP solution with 22% PLA solution was 395 ± 130 nm for 6% and 397 ± 105 nm for 8%, respectively. Despite different concentrations of PVP solutions, both core/shell fibers had an average diameter of about 400 nm and were rather uniform. For the PVP/PLA system, an increase in the concentration of inner solution brought no change in fiber morphology, but resulted in broad distribution of fiber diameters.

Zhang et al.[21] studied the miscibility of PLA and PVP prepared by the casting of a film from mixed polymer solutions of chloroform. Results showed that there was intermolecular interaction between PLA and PVP, detected by Fourier transform infrared spectroscopy, and thus suggested some degree of miscibility of the polymer blend. In this study, core/shell structured ultrafine fibers were produced from PLA and PVP dissolved in miscible solvents. The rate of diffusion of solvents is significantly slower than that in the electrospinning process such that the core/shell morphology is preserved through the process, similar to the result from a previous work.[16]

Flow rate

The solution flow rate for electrospinning is an important controlled variable parameter. Both core and shell solutions should be pumped at appropriate flow rates to prepare the continuous core/shell ultrafine fibers. If the inner solution flow rate is too high, the core fluid jet breaks into droplets. On the other hand, if the outer solution flow rate is too high, the core material cannot be continuous in fibers.[15] Figure 5 shows the TEM micrographs of electrospun PVP/PLA fibers obtained in two pairs of flow rates. For the 6% PVP solution and 22% PLA solution, the typical rate for PVP solution was set at 0.05 mL/h and the feeding rate for PLA solution was 0.1 mL/h. When the inner fluid and the outer fluid flow rate were changed to 0.025 and 0.05 mL/h, respectively, no core/shell structured ultrafine fibers were formed. It was probably because the outer flow rate was too low to wrap the inner solution and thus PVP and PLA solutions were electrospun respectively. It indicated that the flow rates of inner and

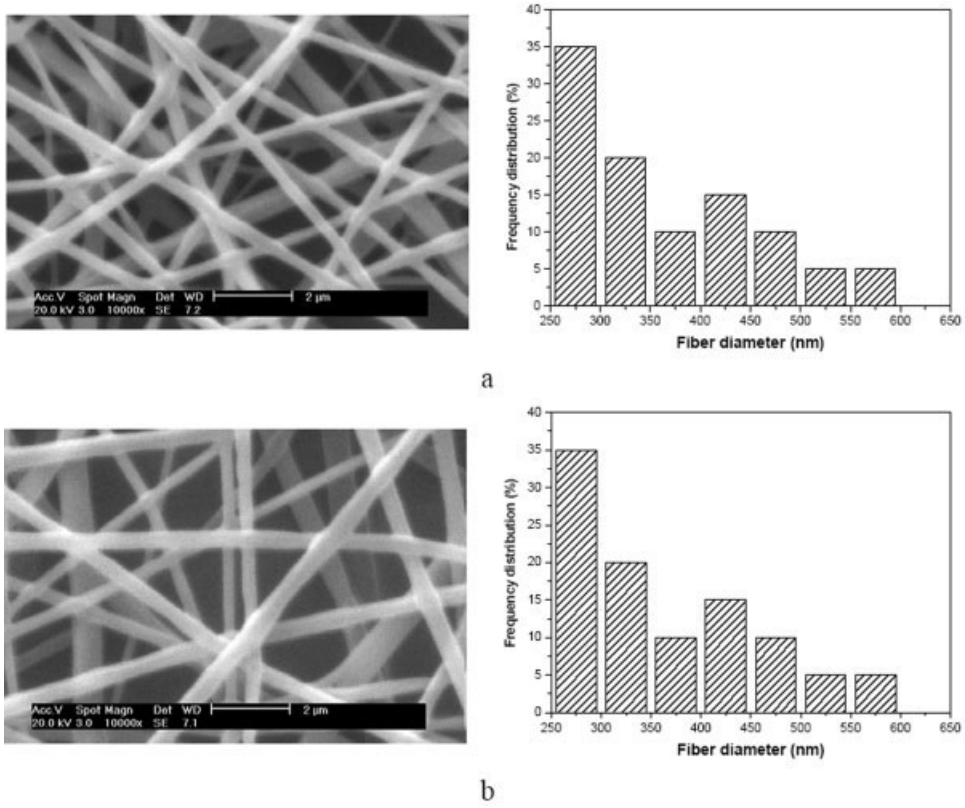

Figure 4 SEM micrographs and diameter distribution of electrospun core/shell fibers from a 22% PLA solution and PVP solutions at different concentrations (×10K): (a) 6%; (b) 8%.

outer polymer solutions were very crucial to the formation of continuous and uniform core/shell fibers.

XPS analysis

XPS analysis has been widely used to study the surface of substances.[22] Since PLA does not possess nitrogen element but PVP does, an absence of N peak on XPS survey spectra will facilitate demonstration of the core/shell structured PVP/PLA fibers. Figure 6 shows the XPS survey spectra of the electrospun ultrafine fibers of pure PVP and PVP/PLA. As XPS analysis could detect elemental information till 10 nm in depth of a sample, the peak of N1s would not appear in the XPS spectra of PVP/PLA core/shell fibers if the PLA shell was thicker than 10 nm. However, the N1s peak at 400 eV was observed in the XPS survey spectra of PVP as well as PVP/PLA in addition to the peaks of C1s and O1s. The N1s peak in Figure 6(b) suggests that some of the core/shell ultrafine fibers might have the half-by-half morphology as shown in Figure 3(c). Otherwise, there might be several pure PVP and PLA electrospun ultrafine fibers formed during the electrospinning process. The nitrogen content obtained from the XPS spectrum of core/shell PVP/PLA ultrafine fibers was 3.6% lower than that of pure PVP (7.5%). This phenomenon may be attributed to the flow instability of the inner fluid and the interfacial instability between the inner and the outer solutions.

Mechanical properties

The tensile stress–strain curves and the mechanical properties of the electrospun PLA and PVP/PLA core/shell fibrous membranes are shown in Figure 7 and Table II. In comparison with the electrospun PLA membrane, the electrospun PVP/PLA membrane gave rise to lower values of the tensile modulus and the tensile strength as well as the elongation. The results indicate that the core/shell PVP/PLA fibrous membrane had good flexibility and deformability. In terms of strength, the introduction of PVP did not provide any strength improvement. It could be attributed to the weak physical interactions among the chains of mixed polymers and the morphology of imperfection. In general, the core/shell structure impacts the stress more than it affects the stain.

Water uptake

The average water uptake of the PLA electrospun nonwoven membranes was (100.5 ± 0.9)%, whereas the value of the PVP/PLA core/shell electrospun nonwoven membranes was (267.8 ± 40.6)%. The large

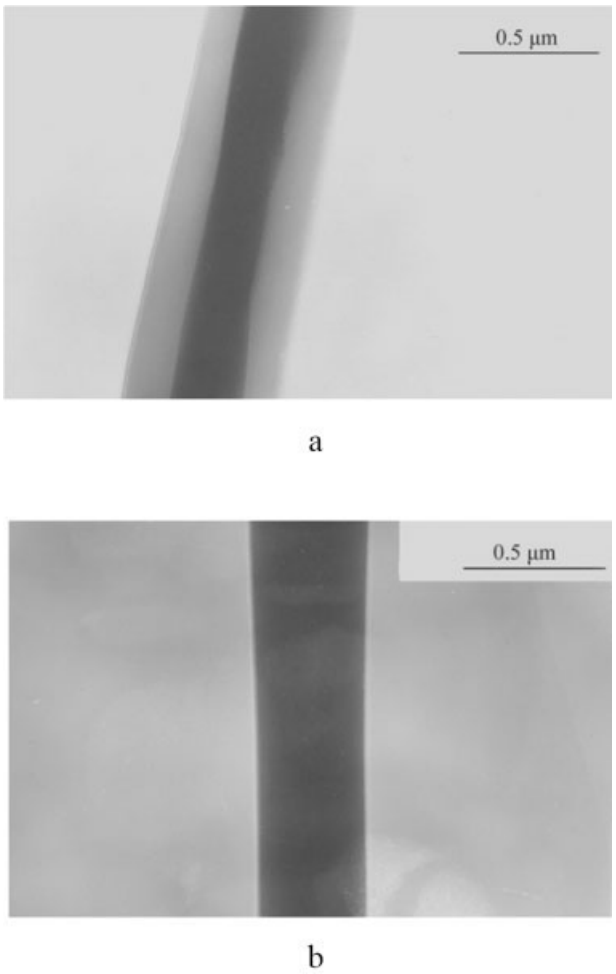

Figure 5 TEM micrographs of the electrospun PVP/PLA fibers obtained in different flow rates (×36K): (a) inner flow rate = 0.05 mL/h, outer flow rate = 0.1 mL/h; (b) inner flow rate = 0.025 mL/h, outer flow rate = 0.05mL/h.

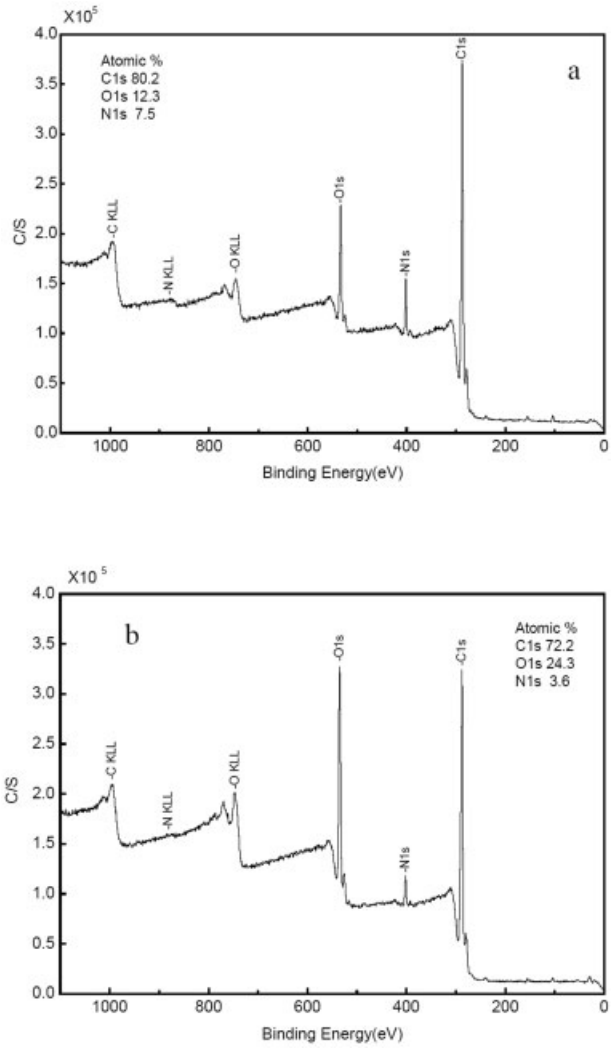

Figure 6 XPS survey spectra of the electrospun membranes: (a) PVP; (b) PVP/PLA.

deviation of the PVP/PLA membrane could be attributed to the half-by-half morphology and the inhomogeneity of core/shell ultrafine fibers. The water uptake of electrospun nonwoven membranes increased dramatically by introducing the core/shell structure. In general, the water uptake values were twice those of the pure PLA fibers membranes because the core/shell structure increased the aspect ratio and specific surface area of the fibers nonwoven membranes.

PVP is a water-soluble polymer, but the results indicate that not all PVP in fibers were dissolved in water. The PLA shell prevented the core from quickly dissolving, and so such core/shell ultrafine fibers may have potential applications in drug release systems and tissue engineering scaffolds for loading bioactive agents.

CONCLUSIONS

Core/shell structured ultrafine fibers of PVP/PLA were prepared by coaxial electrospinning at appropri-

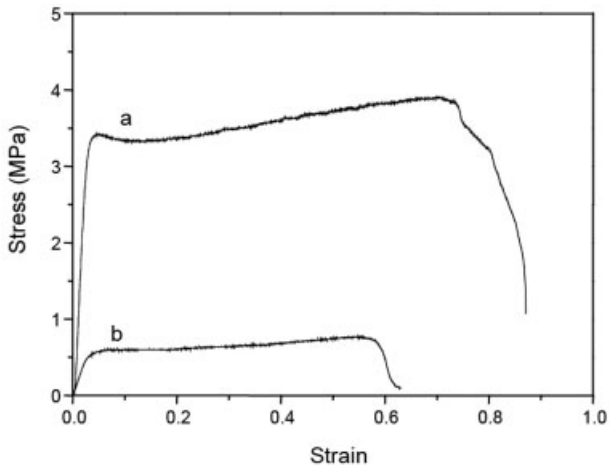

Figure 7 Tensile stress–strain curves of the electrospun membranes: (a) PLA; (b) PVP/PLA.

TABLE II
Mechanical Properties of the Electrospun PLA and PVP/PLA Membranes

Sample	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)
PLA	135.6 ± 12.1	3.88 ± 0.28	88.2 ± 6.3
PVP/PLA	22.4 ± 4.5	0.80 ± 0.08	68.5 ± 9.9

ate conditions, i.e., when the PVP solutions with 6 or 8% concentration was the inner solution at a flow rate of 0.05 mL/h and the outer PLA solution was at a flow rate of 0.1 mL/h. Analyses of TEM and XPS suggested that some of the core/shell ultrafine fibers had the half-by-half morphology and also might contain pure PVP and PLA ultrafine fibers because of bending instability during the electrospinning process. To obtain ideal core/shell ultrafine fibers, the coaxial electrospinning parameters should be further investigated. The results of mechanical properties showed that the tensile strength and tensile modulus of core/shell ultrafine fibers decreased dramatically when compared with those of PLA membrane. It has been found that the water uptake of the core/shell fibrous membranes was more than twice that of the PLA membrane and the core/shell structure prevented the inner component from dissolving into PBS solution.

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