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ORIGINAL CONTRIBUTION

Preparation of electrospun chitosan/poly(vinyl alcohol) membranes

Yuanyuan Zhang · Xiaobo Huang · Bin Duan ·
Lili Wu · Shuo Li · Xiaoyan Yuan

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Abstract Electrospinning of chitosan from its solutions in 2% aqueous acetic acid was studied by adding poly(vinyl alcohol) (PVA) as a “guest” polymer. Properties of the chitosan/PVA solutions including viscosity, conductivity, and surface tension were measured, and effects of the polymer concentration, chitosan/PVA mass ratio and processing parameters (applied voltage, flow rate, capillary-to-collector distance) on the electrospinnability of chitosan/PVA were investigated. Analyses of scanning electron micrographs and transmission electron micrographs suggested that the chitosan/PVA ultrafine fibers were often obtained along with beads, and chitosan was located in the elctrospun fibers as well as in the beads. Uniform chitosan/PVA fibers with an average diameter of 99±21 nm could be prepared from a 7% chitosan/PVA solution in 40:60 mass ratio. Results of Fourier transform infrared spectroscopy and X-ray diffraction demonstrated that there were possible hydrogen bonds between chitosan and PVA molecules, which could weaken the strong interaction in chitosan itself and facilitate chitosan/PVA electrospinnability. The electrospun chitosan/PVA membranes showed higher water uptake and would have potential applications in wound dressings.

Keywords Chitosan · Poly(vinyl alcohol) · Electrospinnability · Morphology · Hydrogen bond

Introduction

Recently, electrospinning, or called electrostatic spinning, has emerged as an efficient technique for preparation of ultrafine fibers with diameters ranging from several nanometers to several microns. Different from traditional methods such as wet spinning, electrospinning process is based on a high-voltage electric field between a metal capillary containing a polymer solution and a ground collector [1, 2]. It has been widely accepted as the simplest and least expensive method to fabricate nanofibers or nanofibrous membranes from a variety of synthetic or natural polymers. The electrospun non-woven membranes exhibit high surface area and porosity. Thus, they may have potential applications such as tissue engineering scaffolds, wound dressings, composite reinforcements, protective clothings, and filters [3–7].

Chitosan, a copolymer of glucosamine and *N*-acetyglucosamine units linked by 1–4 glucosidic bonds, is a cationic polysaccharide obtained by alkaline deacetylation of chitin. Because of its biodegradability, nontoxicity, biocompatibility, and antifungal activity, chitosan and its derivatives have been widely used in the fields of medicine, cosmetics, agriculture, biochemical separation systems, tissue engineering and so on [8–12]. Chitosan fibers, traditionally produced by wet spinning, usually have larger diameters in several microns compared with the electrospun fibers. Blending is an efficacious way to modify spinning behaviors of chitosan. Preparation of blend fibers of chitosan with poly(vinyl alcohol) (PVA) or collagen was ever studied via wet spinning [13, 14]. As a major kind of natural polymers, chitosan is also of great interest in electrospinning. However, because of the strong molecular interaction, it is difficult to successfully electrospin chitosan into uniform ultrafine fibers from its normal solutions in dilute acetic acid.

PVA is a water-soluble polymer with semi-crystalline molecular structure. It shows good properties, such as nontoxicity and chemical stability. Preparation of PVA nano-

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Y. Zhang · X. Huang · B. Duan · L. Wu · S. Li · X. Yuan (✉)
School of Materials Science and Engineering, Tianjin University,
Tianjin 300072, People’s Republic of China
e-mail: yuanxy@tju.edu.cn

fibers by electrospinning has been reported [15–17], and electrospun inorganic nanofibers were often obtained with the help of PVA [18–20].

According to Rutledge et al., electrospinnability of a polymer solution can be defined as the ability to form continuous jets and ultrafine fibers rather than obtaining droplets or beads during electrospinning [21]. The electrospinning phenomenon itself involves basic and significant issues in polymer solutions, in which viscosity, surface tension, and conductivity are the critical factors for the successful preparation of nanofibers by electrospinning. Our previous work showed that poly(ethylene oxide) (PEO) could promote electrospinnability of chitosan in dilute acetic acid solutions [22]. In the present study, another approach was attempted to produce ultrafine chitosan fibers by adding PVA. The electrospinnability of chitosan/PVA was discussed via analyses of scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

Experimental methods

Materials

Chitosan with 90% degree of deacetylation was purchased from Zhejing Yuhuan Ocean Biochemistry, China. The intrinsic viscosity ($[\eta]$) was measured by an Ubbelohde viscometer, and the viscosity-average molecular weight of chitosan (165 kDa) was calculated in terms of Mark–Houwink equation $[\eta] = K\,\overline{M}_{\eta}^{\alpha}$, where $K = 1.81 \times 10^{-3}$ ml/g, α=0.93 [23]. PVA, with degree of polymerization of 1750±50 and degree of hydrolysis of 98%, was purchased from Tianjin Chemical, China. Chitosan and PVA were used without further purification.

Preparation and properties of chitosan/PVA solutions

The polymer concentration (%) was determined by the percentage of chitosan (g) or total mass (g) of chitosan and PVA in the solvent (ml). Chitosan solutions were prepared by dissolving the powdered materials in 0.2 M acetic acid at room temperature under a magnetic stir for 1 h. PVA was also dissolved in 0.2 M acetic acid at 80 °C under stirring for 1 h. After cooling to room temperature, a given amount of the chitosan solution was mixed with the PVA solution in a certain chitosan/PVA mass ratio and then, the mixture was continuously stirred for 1 h. The solution viscosity was determined by a rotating viscometer (Model NDJ-79, Shanghai, China). The solution surface tension was measured in the Wilhelmy plate method with a tensiometer (DCAT 21, Dataphysics, Germany). The solution conductivity was tested in a conductivity instrument (Model DDS-11A, Shanghai, China).

Electrospinning

Electrospinning was carried out in the air. The schematic setup of electrospinning was the same as described in our previous report [22]. The flow rate of the chitosan/PVA solution was controlled by a syringe pump (Zhejiang University Medical Instrument, China), which could be adjusted in the range of 0.1–99.9 ml/h. The polymer solution was put in a 20-ml glass syringe equipped with a capillary (ID=0.8 mm) connected with an applied voltage power supply (Tianjin University, China). The collector was a grounded circular copper plate covered with a piece of aluminum foil.

Characterization

The electrospun membranes were viewed under a scanning electron microscope (Philips XL-30) after gold coating and a transmission electron microscope (Philips Tecnai G2 F20) equipped with electron diffraction spectrometry (TEM-EDS). For TEM observation, the polymer solution was electrospun directly onto a copper mesh. The diameter of electrospun fibers was measured using image analyzer (Adobe Photoshop7.0) from SEM micrographs in original magnifications of 10 k×. FTIR spectra were recorded using a BIO-RAD FT-3000 spectrometer. The XRD measurement was carried out by a wide-angle X-ray diffractometer (D/MAX-2500, Rigaku, Japan) at a 2θ scanning rate of 3°/min in the range of 5°–50°.

Electrospun chitosan/PVA membranes were cut into pieces in 2×2 cm and weighed in an electronic balance with a 0.1-mg resolution. After incubation in distilled water at room temperature for 2 h, the samples were weighed again immediately after removing them from water and absorbing surface water with a piece of filter paper. The water uptake of the electrospun membranes was calculated using the following equation:

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

where, m_0 and m_1 were the masses of the membranes before and after the incubation of the samples in water, respectively.

Results and discussion

As chitosan could not be easily electrospun in its dilute acetic acid solutions, blending with another polymer was supposed to interfere with the strong interaction between the chitosan macromolecules so as to improve its electrospinnability. Based on this hypothesis, we have tested that PEO could facilitate the chitosan electrospinning process [22]. In the present study, PVA was introduced as a "guest" polymer because PVA was also assumed to show interactions with chitosan through hydrogen bonding at a molecular level via amino or hydroxyl groups. Another reason was that PVA could be conveniently electrospun from its aqueous solutions. Electrospinnability of chitosan/PVA was studied by the analysis of the solution properties including surface tension, viscosity, and conductivity, which would have effects on the morphology of the electrospun fibers. These solution properties were mainly related to the system parameters such as the solution concentration and the mass ratio of chitosan to PVA. So, the polymer concentration and the chitosan/PVA mass ratio in the blend solutions were particularly examined. The processing parameters including the applied voltage, the flow rate, and the capillary-to-collector distance were also studied.

Effect of system parameters on morphology

Concentration of chitosan/PVA

Figure 1 shows SEM micrographs suggesting the effect of the polymer concentration on the morphology of the electrospun chitosan/PVA fibers. Drastic morphological changes were found as the concentration increased. Varying the chitosan/PVA concentration from 4 to 8%, the solution viscosity increased from 2.45 to 20.0 Pa·s as shown in Table 1 (nos. 1–4). Little fibers with a lot of beads were obtained from the 4% chitosan/PVA solution (Fig. 1a). The bead-fiber morphology was attributed to the lower viscosity of the polymer solution. When the concentration of the chitosan/PVA solution increased to 6 or 7%, the fibers were gradually elongated, and ultrafine fibers with spindle-like beads were formed (Fig. 1b,c). If the concentration of the chitosan/PVA solution was further increased to 8%, only a few electrospun fibers with larger diameters (Fig. 1d) were obtained for the higher solution viscosity. The weak

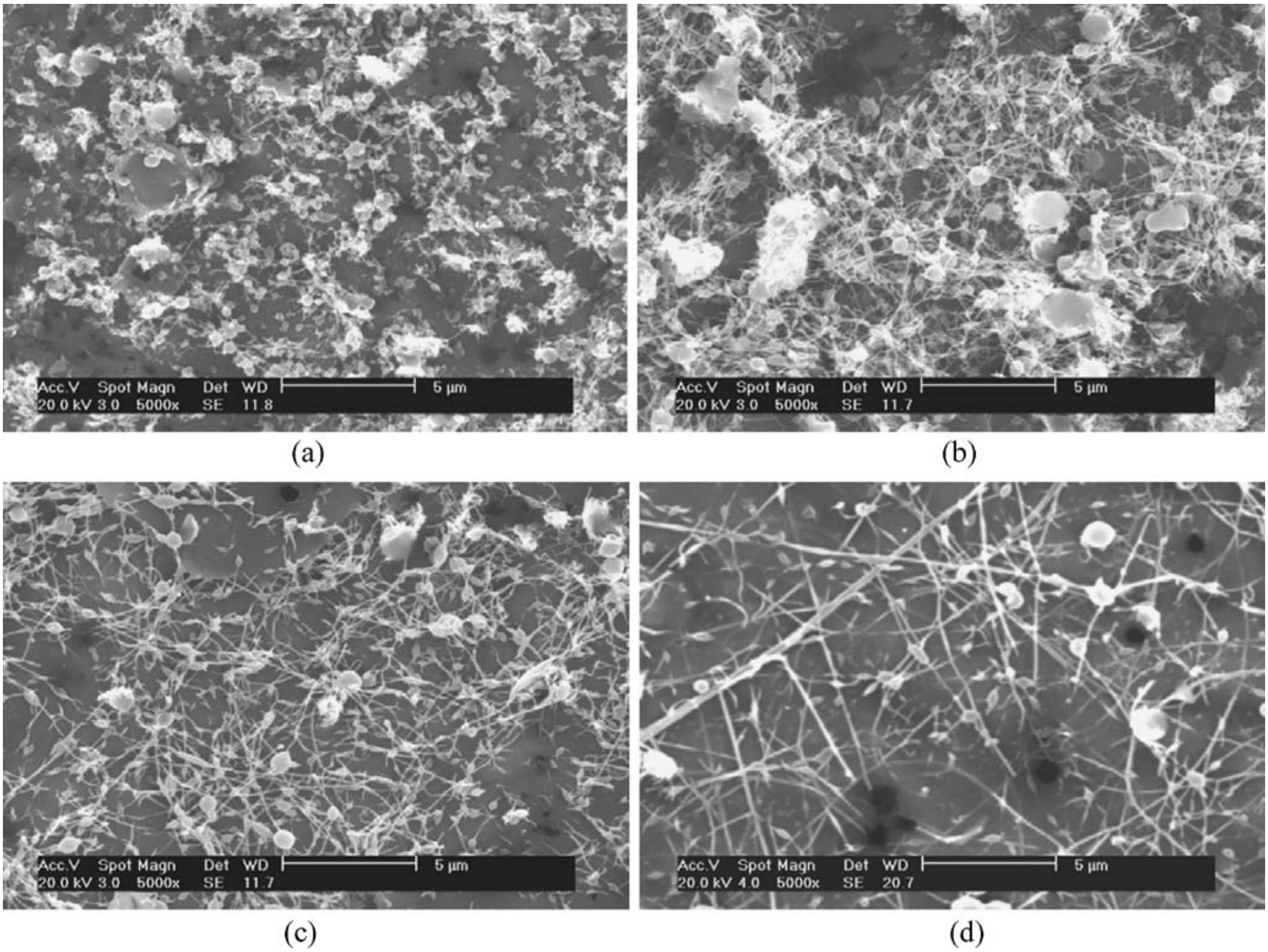

Fig. 1 SEM micrographs of electrospun chitosan/PVA obtained from their solutions in 50:50 mass ratio at different concentrations. **a** 4%; **b** 6%; **c** 7%; **d** 8%. Voltage, 15 kV; flow rate, 0.12 ml/h; distance, 10 cm

Table 1 Properties of chitosan and PVA solutions

Number	Concentration (%)	Chitosan/PVA mass ratio	Conductivity (mS/cm)	Surface tension (mN/m)	Viscosity (Pa·s)
1	4	50:50	2.90	63.42	2.45
2	6	50:50	4.20	58.84	7.15
3	7	50:50	4.40	61.19	8.30
4	8	50:50	13.50	57.06	20.0
5	7	20:80	2.40	58.64	8.25
6	7	40:60	4.10	61.00	8.30
7	7	60:40	4.80	58.34	9.55

The solvent is 2% acetic acid solution with conductivity of 0.95 mS/cm.

molecular mobility under the higher viscosity made the electrospun jets difficult to deform and split. As a result, the chitosan/PVA solutions with concentration higher than 8% could not be smoothly electrospun.

Chitosan/PVA mass ratio

The morphology of the electrospun chitosan/PVA fibers prepared from 7% solutions with different mass ratios is shown in Fig. 2. When the mass ratio of chitosan/PVA was 20:80 or 40:60, ultrafine fibers with average diameters around 100 nm (Fig. 2a,c) were obtained in spite of a few beads. The beads-on-string morphology of electrospun fibers could also be observed more clearly from the TEM images (Fig. 2b,d). When the mass ratio of chitosan/PVA was 50:50 (Fig. 2e,f), the electrospinning process was stable, but a mass of beads were found. Beads were only obtained (Fig. 2g) when the mass ratio of chitosan/PVA increased to 60:40. If the mass ratio of chitosan/PVA was further higher than 80:20, the blend solutions could not be electrospun for the higher amount of chitosan in the solution.

As shown in Table 1 (nos. 3, 5–7), it can be seen that the solution properties did not exhibit significant changes when the mass ratio of chitosan/PVA altered from 20:80 to 60:40. The solution viscosity and the conductivity of the chitosan/PVA solutions increased slightly from 8.25 to 9.55 Pa·s and from 2.4 to 4.8 mS/cm, respectively. The surface tension of the solutions varied in the range from 58 to 61 mN/m. It was assumed that the hydrogen bonding between PVA and chitosan molecules could possibly happen in addition to the interactions between chitosan macromolecules themselves, so that the blend solutions of chitosan/PVA showed better electrospinnability. The verification was further conducted by analyses of FTIR and XRD.

From the above results, the concentration and the mass ratio of chitosan/PVA solutions were the two important parameters which had remarkable effects on the morphology of electrospun chitosan/PVA fibers. To obtain uniform electrospun fibers, it was necessary to control the chitosan/PVA concentration in 6–7% and the mass ratio of chitosan/PVA less than 50:50.

To further determine the composition of the electrospun fibers and beads, TEM-EDS analysis was performed. The element compositions in the electrospun fibers and beads are shown in Table 2. It exhibited all of the fibers and beads obtained from chitosan/PVA solutions with 20:80, 40:60, and 50:50 mass ratios carbon, oxygen, and nitrogen, and the nitrogen amount in beads was more than that in fibers even when the original solution composition of chitosan to PVA was 20:80. From the chemical structure of chitosan and PVA, it could be thought that the oxygen percentage was from the hydroxyl groups in chitosan or PVA, and the nitrogen percentage belonged to the $-NH_2$ groups, and a small amount of $-NHCOCH_3$ groups in chitosan. Therefore, the above results indicated that chitosan was distributed in both fibers and beads, but the chitosan amount in beads was more than its amount in fibers. It was also suggested that PVA was possibly distributed as a separated phase, and chitosan existed probably in a continuous phase in the electrospun fibers and beads, similar to the result reported by Li and Hsieh [24].

Effect of process parameters on morphology

Voltage

The voltage was a processing parameter that could influence the electrospinning process. In this study, the electrospinning process of a 7% chitosan/PVA solution with 40:60 mass ratio was all stable. When the voltage increased from 10 to 20 kV, as shown in Fig. 3, the morphology of electrospun chitosan/PVA fibers exhibited a slight change, and the electrospun fibers were pretty uniform. The electrospun fiber diameters were varied mostly from 50 to 200 nm, and the average fiber diameter was 99±26 nm when the voltage was 15 kV. The result showed that the voltage had a little effect on the electrospinnability of chitosan/PVA. Similar results were ever obtained during electrospinning of polysulfone in our previous study [25].

Distance

Figure 4 shows the SEM micrographs illuminating the influence of the capillary-to-collector distance on the morphology of the electrospun chitosan/PVA fibers. When the distance was 10 cm, the diameter of the electrospun chitosan/PVA fibers was in the range of 50 to 150 nm, with an average diameter of 114±35 nm (Fig. 4a). As for 15-cm distance, the number of bead decreased, whereas the fiber diameter also ranged in 50–150 nm, with a smaller average

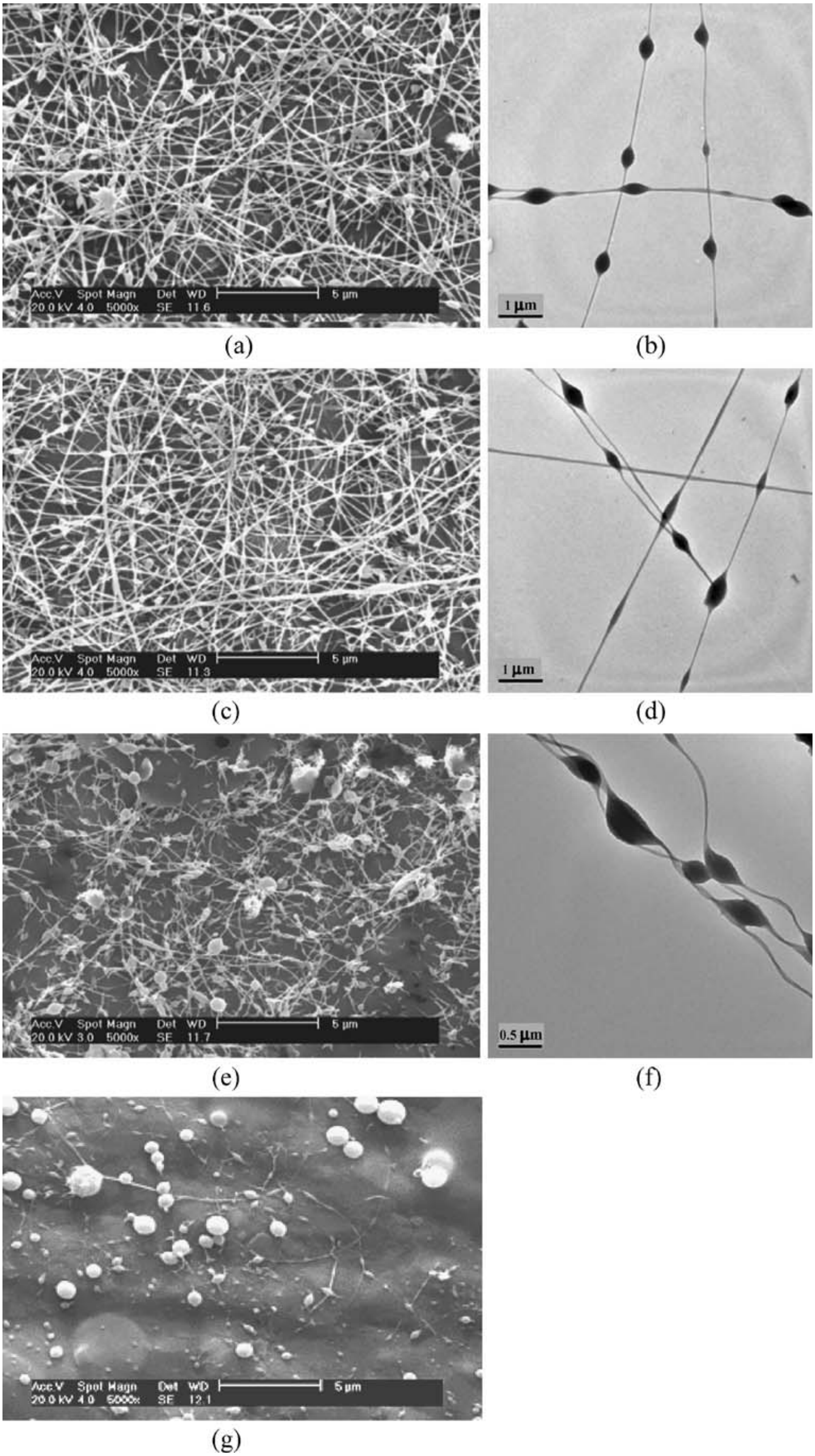

Fig. 2 SEM (**a**, **c**, **e**) and TEM (**b**, **d**, **f**) micrographs of electrospun chitosan/PVA obtained from their 7% solutions in different mass ratios. **a**, **b** 20:80; **c**, **d** 40:60; **e**, **f** 50:50; **g** 60:40. Voltage, 15 kV; flow rate, 0.12 ml/h; distance, 10 cm

Table 2 Composition data (mean±standard deviation) of fibers and beads by TEM-EDS

Chitosan/PVA mass ratio		C (at.%)	N (at.%)	O (at.%)
20:80	Bead	86.20±2.78	6.14±2.54	5.52±0.73
	Fiber	86.94±6.26	1.92±1.20	4.86±0.08
40:60	Bead	80.87±2.00	6.45±0.32	8.85±1.42
	Fiber	86.02±1.34	2.11±1.05	5.82±0.38
50:50	Bead	81.31±0.72	2.74±1.20	11.21±1.05
	Fiber	87.81±0.84	0.73±0.32	7.50±0.97

diameter of 99±21 nm (Fig. 4b). Increasing the capillary-to-collector distance could provide longer time for the solvent to evaporate, and the charged fluid could be split for more times so that smaller electrospun fibers were obtained.

Flow rate

As shown in Fig. 5, when the solution flow rate increased from 0.06 to 0.24 ml/h, the morphology and the diameter distribution of the electrospun chitosan/PVA fibers did not show obvious changes. The diameters of the electrospun chitosan/PVA fibers were mostly in the range of 50 to 200 nm. The average diameters of the electrospun fibers measured from SEM micrographs were 105±21 nm (Fig. 5a), 99±21 nm (Fig. 5b), and 106±27 nm (Fig. 5c) when the flow rates were 0.06, 0.12, and 0.24 ml/h, respectively. It showed that the flow rate did not remarkably influence the morphology of the electrospun chitosan/PVA fibers either.

FTIR analysis

Figure 6 shows FTIR spectra of the electrospun fibrous membranes prepared from 7% chitosan/PVA solutions in 20:80, 40:60, 50:50, and 60:40 mass ratios, respectively, along with the raw materials of chitosan and PVA. In the FTIR spectrum of chitosan (Fig. 6a), the absorption peak of carbonyl stretching vibration in O=C–NHR groups was observed at 1664 cm^{-1}, and the absorption peak at 1593 cm^{-1} was attributed to N–H bending vibration in amine groups [26]. The absorption peaks of O–H and N–H stretching vibrations appeared at 3,449 cm^{-1} [26]. As shown in Fig. 6f, PVA exhibited stretching vibration peak of its side hydroxyl groups at 3,413 cm^{-1}.

With the addition of PVA, the absorption peak at 3,449 cm^{-1} in the FTIR spectra of the electrospun chitosan/PVA membranes became sharp (Fig. 6b–e) and shifted to the lower wave numbers. The absorption peak at 1,593 cm^{-1} of amino groups gradually decreased and finally disappeared due to the decreasing amount of chitosan in electrospun membranes as well as the interaction between PVA and chitosan macromolecules. It suggested that hydrogen bonds between hydroxyl groups in

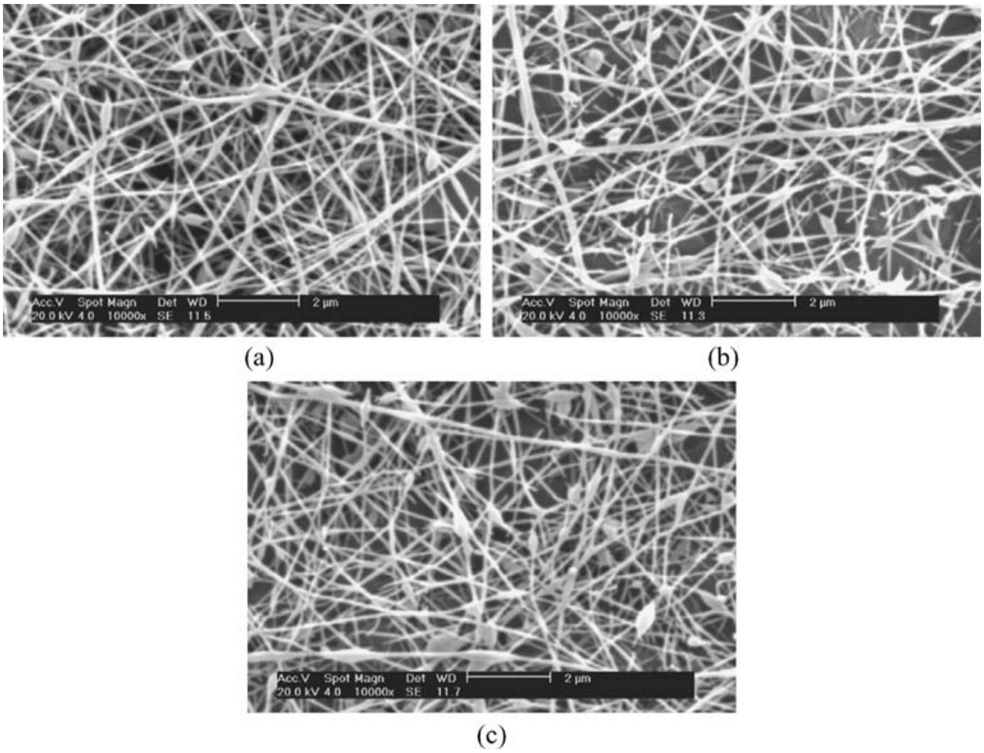

Fig. 3 SEM micrographs of electrospun chitosan/PVA from their 7% solutions in 40:60 mass ratio at different voltages. **a** 10 kV; **b** 15 kV; **c** 20 kV. Flow rate, 0.12 ml/h; distance, 10 cm

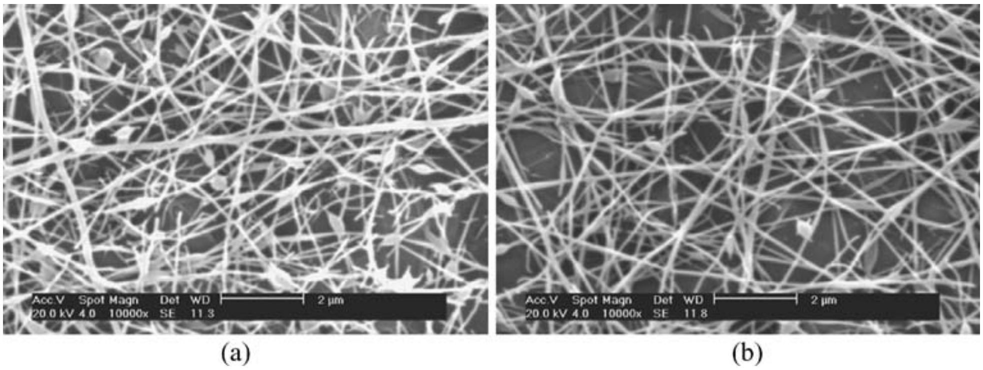

Fig. 4 SEM micrographs of electrospun chitosan/PVA from their 7% solutions in 40:60 mass ratio at different distances. **a** 10 cm; **b** 15 cm. Voltage, 15 kV; flow rate, 0.12 ml/h

PVA and amino groups or hydroxyl groups in chitosan could possibly come into play. Therefore, the addition of PVA could moderate the interaction between chitosan macromolecules and, thus, improved the electrospinnability of chitosan with PVA. The following analysis of XRD could further confirm this assumption.

XRD analysis

The XRD patterns of the same specimens as those in the FTIR measurement are shown in Fig. 7. According to references [27, 28], chitosan showed crystalline peaks at 2θ of 10.5°, 15.4°, and 20.1° and the PVA diffractions exhibited at 2θ of 10° and 19.8°. In this study, crystalline peaks at 2θ of 10.3° (100), 15.2° (002), 19.8° (020), and 21.9 (102) were found in the XRD pattern of the raw chitosan (Fig. 7a). And, the XRD pattern of the raw PVA (Fig. 7f) composed of obvious crystalline peaks at 2θ of 11.3° (100), 19.4° (101), 22.8° (200), and 40.6° (111) [29]. In Fig. 7b, in the case of 20:80 mass ratio of chitosan/PVA, two crystalline peaks were also found at 2θ of around 19° and 22°, but the peak at 19° disappeared when the chitosan amount further increased. With increasing PVA amount, the chitosan crystalline peak at 10.3° also faded out. It suggested that the crystallinity of chitosan/PVA fibers with higher chitosan amounts (40:60, 50:50, 60:40 mass ratios) became lower in comparison with the electrospun PVA or 20:80 chitosan/PVA membranes. The decrease of the crystallinity of the electrospun chitosan/PVA membranes was probably attributed to the hydrogen bonding interaction between chitosan and PVA macromolecules.

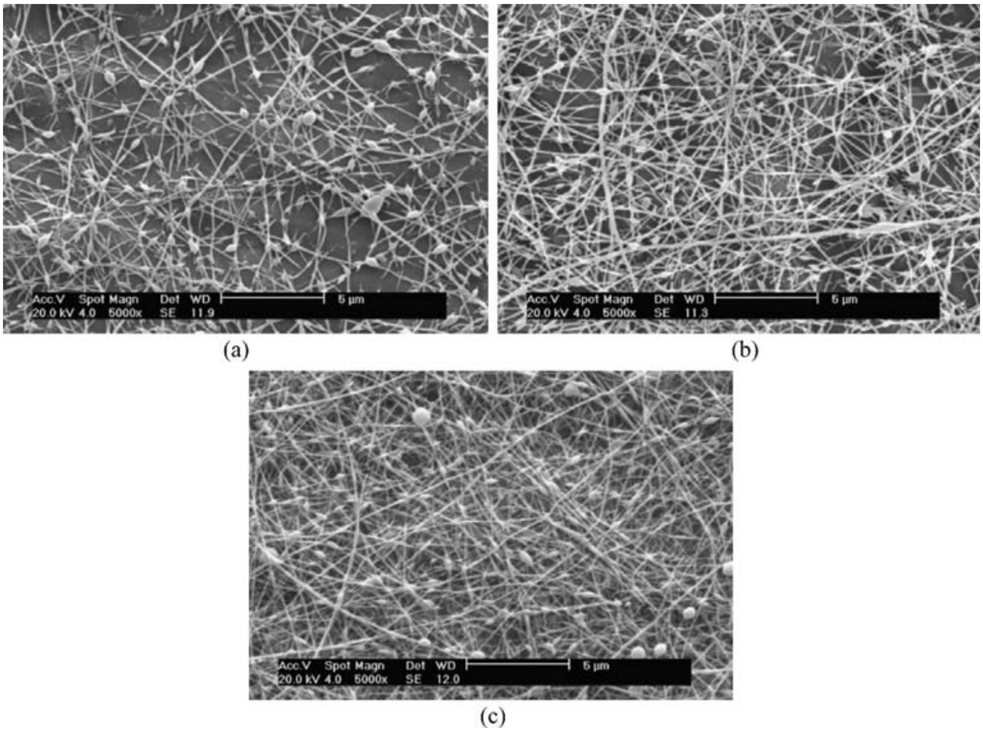

Fig. 5 SEM micrographs of electrospun chitosan/PVA from their 7% solutions in 50:50 mass ratio at different flow rates. **a** 0.06 ml/h; **b** 0.12 ml/h; **c** 0.24 ml/h. Voltage, 15 kV; distance, 10 cm

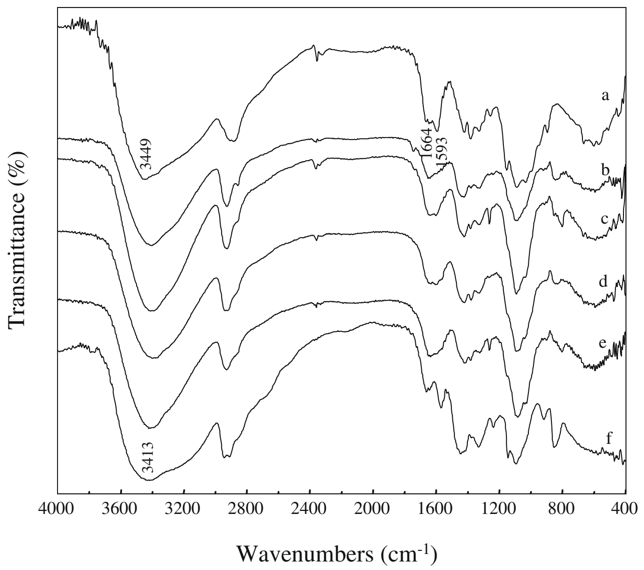

Fig. 6 FTIR spectra of electrospun chitosan/PVA membranes from their 7% solutions with different mass ratios. **a** Raw chitosan; **b** 20:80; **c** 40:60; **d** 50:50; **e** 60:40; **f** raw PVA. Voltage, 15 kV; flow rate, 0.12 ml/h; distance, 10 cm

Results of XRD and FTIR indicated that PVA could possibly have interactions with chitosan through hydrogen bonding between hydroxyl groups in PVA and amino or hydroxyl groups in chitosan. Therefore, the strong molecular interactions and the crystalline structure of chitosan were interfered by the addition of PVA. Subsequently, the electrospinnability of chitosan with PVA was greatly improved.

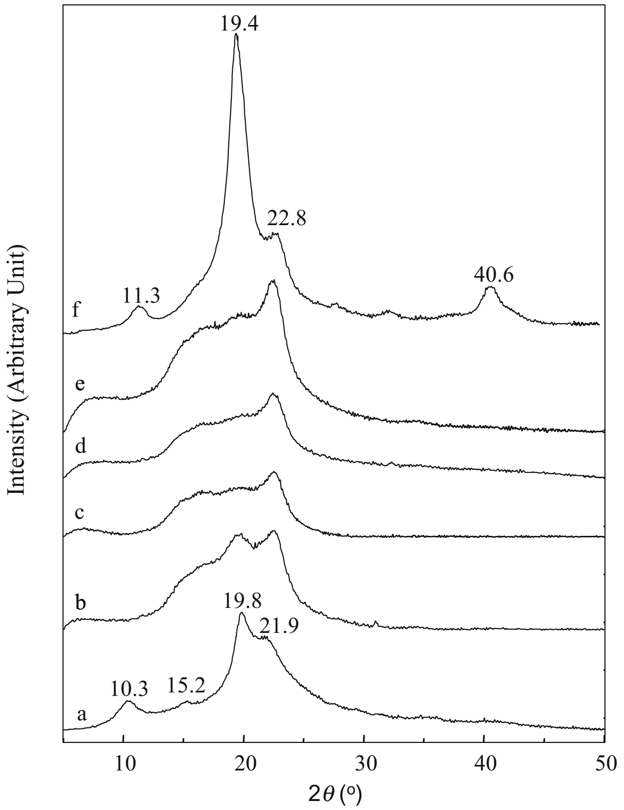

Fig. 7 XRD patterns of electrospun chitosan/PVA membranes from their 7% solutions with different mass ratios. **a** Raw chitosan; **b** 20:80; **c** 40:60; **d** 50:50; **e** 60:40; **f** raw PVA. Voltage, 15 kV; flow rate, 0.12 ml/h; distance, 10 cm

Water uptake

Figure 8 illustrates the variation of the water uptake of the electrospun chitosan/PVA membranes with different mass ratios. It suggested that the water uptake increased from 27.6 to 151.6% when the mass ratio of chitosan/PVA was changed from 60:40 to 20:80. Because PVA is an excellent water-soluble polymer, the water uptake of the electrospun chitosan/PVA memebranes could get higher with the increasing amount of PVA. However, the better nanofibrous morphology of the electrospun chitosan/PVA membranes with higher PVA amount (Fig. 2a,c), which exhibited higher surface-to-volume ratio and porosity, could be the main reason to make their water uptake increase. The electrospun chitosan/PVA memebranes with higher water uptake would have potential applications in wound dressings.

Conclusions

Ultrafine chitosan fibers could be produced by electrospinning via the addition of PVA in the chitosan/dilute acetic acid solutions. The polymer concentration and the chitosan/PVA mass ratio were two important factors influencing the electrospinnability of the chitosan/PVA solutions as well as the morphology of the electrospun membranes. Uniform chitosan/PVA fibers with an average

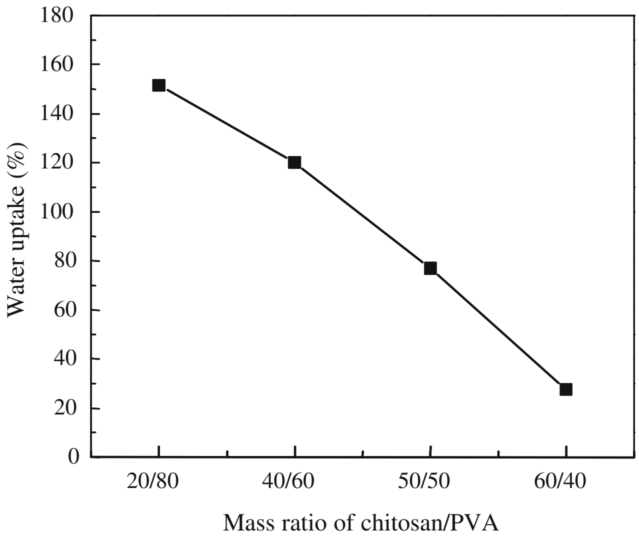

Fig. 8 Water uptake of electrospun chitosan/PVA membranes from their 7% solutions with different mass ratios. Voltage, 15 kV; flow rate, 0.12 ml/h; distance, 10 cm

diameter of 99±21 nm were prepared from a 7% chitosan/PVA solution in 40:60 mass ratio. Results of TEM-EDS showed that both electrospun fiber and bead contained nitrogen and exhibited the existence of chitosan in both fibers and beads. Analyses of FTIR and XRD suggested that hydrogen bonding between chitosan and PVA molecules may occur so that electrospinnability of chitosan/dilute acetic acid solutions was improved with the help of PVA. The electrospun chitosan/PVA membranes could have potential applications in wound dressings because of their higher water uptake.

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