

Poly(vinyl alcohol)/Chitosan Oligosaccharide Blend Submicrometer Fibers Prepared from Aqueous Solutions by the Electrospinning Method

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ABSTRACT: Submicrometer fibers of poly(vinyl alcohol) (PVA) and chitosan oligosaccharide [COS; i.e., (1→4)-2-amino-2-deoxy-β-D-glucose] were prepared by an electrospinning method with aqueous solutions with polymer concentrations of 7.5–15 wt %. Scanning electron microscopy, Fourier transform infrared, X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis were used to characterize the morphology and properties of the PVA/COS fibers. The PVA/COS mass ratio, the total polymer concentration, and processing parameters such as the applied voltage and capillary-to-

collector distance played important roles in controlling the fiber morphology. Fourier transform infrared and X-ray diffraction data demonstrated that there were possibly hydrogen bonds between COS and PVA molecules that weakened the interactions in COS and improved the electrospinnability of PVA/COS. Moreover, with a higher percentage of COS in the PVA/COS blend fibers, superior thermal stability could be obtained. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 132–140, 2009

Key words: biofibers; blends; fibers

INTRODUCTION

The electrospinning technique has attracted great interest among academic and industrial scientists because it is a very simple and effective approach to producing nanofibers, which have been found to be attractive for various applications in biomedical engineering, filtration, protective clothing, catalysis reactions, and sensors.^{1–5} In a typical electrospinning process, a high voltage is applied to create electrically charged jets of polymer solutions. The principle of the electrospinning method is quite simple: the electrostatic field stretches the polymer solution into fibers as the solvent is evaporating. However, the process is difficult to control, and several variables have an influence on the properties of the end product. Furthermore, the quality of the fibers is typically inconsistent. For example, the fiber deposition may be uneven, or the distribution of the fiber diameter may be large. Doshi and Reneker⁶ reported the main

principle of the electrospinning technique. In an electrospinning process, a polymer solution, held by its surface tension at the end of a capillary tube, is subjected to an electric field. Charge is induced on the liquid surface by an electric field. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone.⁷ When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Because this jet is charged, its trajectory can be controlled by an electric field. As the jet travels in air, the solvent evaporates, leaving behind a charged polymer fiber, which lies randomly on a collecting metal screen.

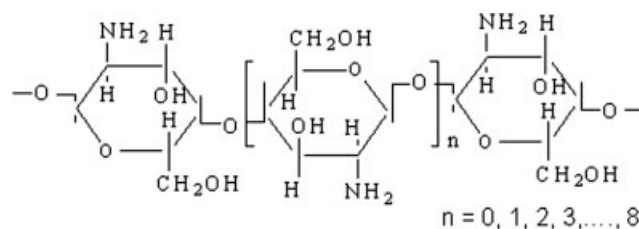
Poly(vinyl alcohol) (PVA) is a water-soluble polymer produced industrially by the saponification of poly(vinyl ester) or poly(vinyl ether), and it is a semicrystalline hydrophilic polymer with good chemical and thermal stability.⁸ PVA is highly biocompatible and nontoxic. It can be processed easily and has high water permeability.⁹ PVA solutions can form physical gels from various types of

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solvents. These properties have led to the use of PVA in a wide range of applications in the medical, cosmetic, food, pharmaceutical, and packaging industries. PVA-containing solutions have been processed by numerous techniques, including sol-gel processing, phase separation, and freeze-thaw cyclic treatments. Ultrafine PVA fibers, which may have different potential applications than microfibers, cannot be produced by conventional spinning techniques. It has been reported that common methods, such as melt spinning and dry or wet spinning, can be used to prepare only fibers with diameters ranging from 5 to 500 μm .¹⁰ It is known that electrospinning is a straightforward method for preparing fibers with diameters as small as several tens of nanometers. Several nanofibers, from either a pure polymer or a polymer blend, have been prepared with the electrospinning technique in past years.^{3,6,11–16} Crosslinked PVA fiber mats were prepared by electrospinning, and the crystallinity, water solubility, and mechanical properties of the mats were studied by Ding et al.¹¹ Electrospun fiber mats of organic-inorganic hybrids such as PVA/silica and PVA/ $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ were prepared and characterized by Shao et al.⁸ and Gong et al.,¹⁷ respectively. The effect of the molecular weight on electrospun fibrous PVA was discussed by Koski et al.¹⁶ Stabilization of fully hydrolyzed PVA fibers by a treatment with methanol was investigated by Yao et al.¹⁸

On the other hand, chitosan is an N-deacetylated derivative of chitin, the second most abundant polysaccharide in nature after cellulose. It is generally regarded as nontoxic, biocompatible, and biodegradable.¹⁹ It has many unique functional properties for different applications requiring a high molecular weight, high viscosity, high crystallinity, and capacity to hydrogen-bond intermolecularly, but its insolubility at physiological pH values (7.2–7.4) and rigid D-glucosamine structures lead to the poor solubility of chitosan in common organic solvents and in water, restricting its uses, especially in the human body. However, the chitosan depolymerization products, that is, low-molecular-weight chitosan [chitosan oligosaccharide (COS)], could overcome these limitations and hence find much wider applications in diversified fields.²⁰ Structurally, chitosan is a deacetylated derivative of chitin combined with β -1 and 4 of N-acetyl glucosamine, and COS is a saccharide of glucosamine hexaose from 2 to 10 with a chemical structure characteristic of chitosan, as shown in Scheme 1. Nanofibrous chitosan-containing hybrid materials have been electrospun from mixed solutions of chitosan and poly(ethylene oxide),^{21,22} chitosan and silk fibroin,²³ chitosan and PVA,^{24–27} N-carboxyethylchitosan and polyacrylamide, and N-carboxyethylchitosan and PVA.^{28,29} However, to the best of our knowledge, water-soluble chitosan derivatives (i.e., COS with PVA), used for improving



Scheme 1 Chemical structure of COS.

fiber uniformity, especially for electrospinning processability in dilute solutions, have not been reported yet.

In this work, we used COS and PVA as the model components in aqueous solutions to demonstrate the effects of electrospinning instrument parameters, including the electric voltage and tip-to-target distance, and solution parameters, such as the polymer concentration and feed mass ratio, on improving the uniformity of electrospun PVA/COS blend submicrometer fibers. Optimum electrospinning conditions were deduced with the help of a series of characterization methods, including scanning electron microscopy (SEM), Fourier transform infrared (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and mechanical property measurement.

EXPERIMENTAL

Materials

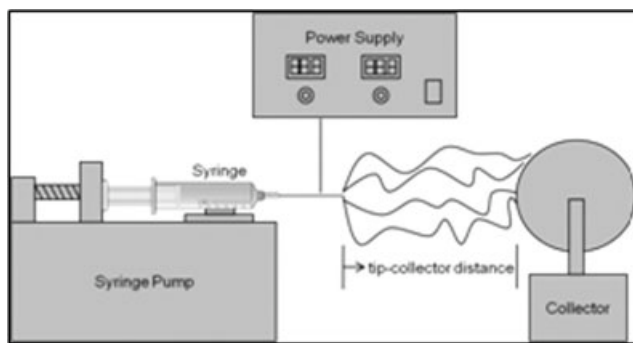
PVA with a number-average degree of polymerization of 1700 (fully hydrolyzed, degree of saponification = 99.9%) was obtained from DC Chemical Co. (Seoul, Korea), and COS (average molecular weight > 10,000, 100% water-soluble) was purchased from Kittolife Co. (Kyongki-Do, Korea) and used without further purification. Doubly distilled water was used as a solvent for preparing all polymer solutions.

Preparation of the PVA/COS blend solutions

PVA was dissolved in doubly distilled water at 80°C under magnetic stirring for 2 h and then cooled to room temperature. COS powder was dissolved also in the doubly distilled water under magnetic stirring for 2 h at room temperature. The PVA/COS blend solutions were prepared through the mixing of bulk PVA and COS aqueous solutions at total concentrations of 7.5–15 wt % at room temperature with gentle stirring for another 2 h.

Electrospinning of the PVA/COS blend submicrometer fibers

During electrospinning, high-voltage power (model CPS-60K02VIT, Chungpa EMT Co., Ltd., Seoul, Korea) was applied to the PVA/COS solution in a



Scheme 2 Schematic representation of the electrospinning technique.

syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted at 5–20 kV. The solution was delivered to the blunt needle tip via a syringe pump to control the solution flow rate. Fibers were collected on electrically grounded aluminum foil placed at a 5–20-cm vertical distance to the needle tip. A schematic of the instrumentation used for the electrospinning process is shown in Scheme 2.

Characterization

The morphology and property characterization of the electrospun PVA/COS submicrometer fibers was conducted with a field-emission scanning electron

microscope (model JSM-6380, JEOL) after gold coating, an FTIR instrument (IFS 120HR, Bruker), and an X-ray diffractometer (X'Pert APD, Philips) with Cu K α radiation and a wave number of 0.154 nm. The scanning rate was 2°/min, and the range was 10–30° (2 θ). The fiber diameter was measured from the field-emission SEM images, and five images were used for each fiber sample. From each image, at least 20 different fibers and 100 different segments were randomly selected, and their diameters were measured to generate an average fiber diameter with Photoshop 5.0 software. The thermal behavior of the PVA fibers was studied with DSC (model Q-10; TA Instruments, United States) and TGA techniques (model Q-50; TA Instruments). The tensile strength was determined with a Zwick (Germany) Z005 material testing machine.

RESULTS AND DISCUSSION

Because of the various advantages of PVA and chitosan polymer, the preparation of electrospun PVA/chitosan composite materials has been investigated by many researchers. In this study, for the first time, the blending of PVA and COS aqueous solutions was used in electrospinning to prepare submicrometer nanofibers. To obtain the optimized electrospinning conditions for thinner and uniform PVA/COS fibers, we conducted a series of experiments with

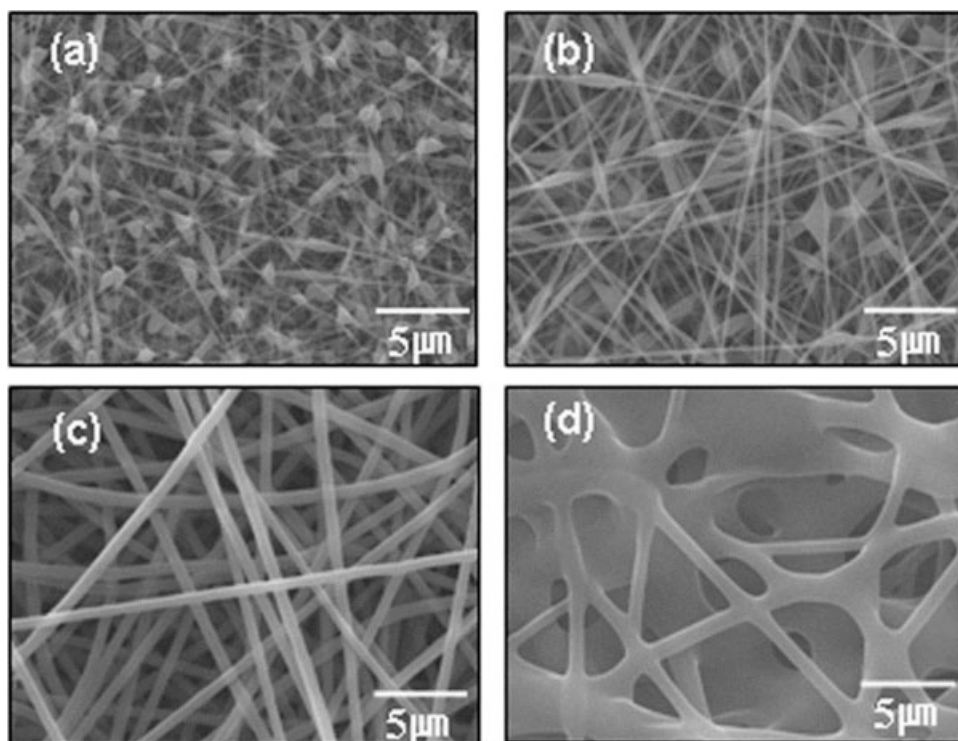


Figure 1 SEM images of electrospun PVA/COS blend submicrometer fibers synthesized with various voltages: (a) 5, (b) 10, (c) 15, and (d) 20 kV (total polymer concentration of PVA and COS = 12.5 wt %, PVA/COS mass ratio = 8/2, TCD = 15 cm).

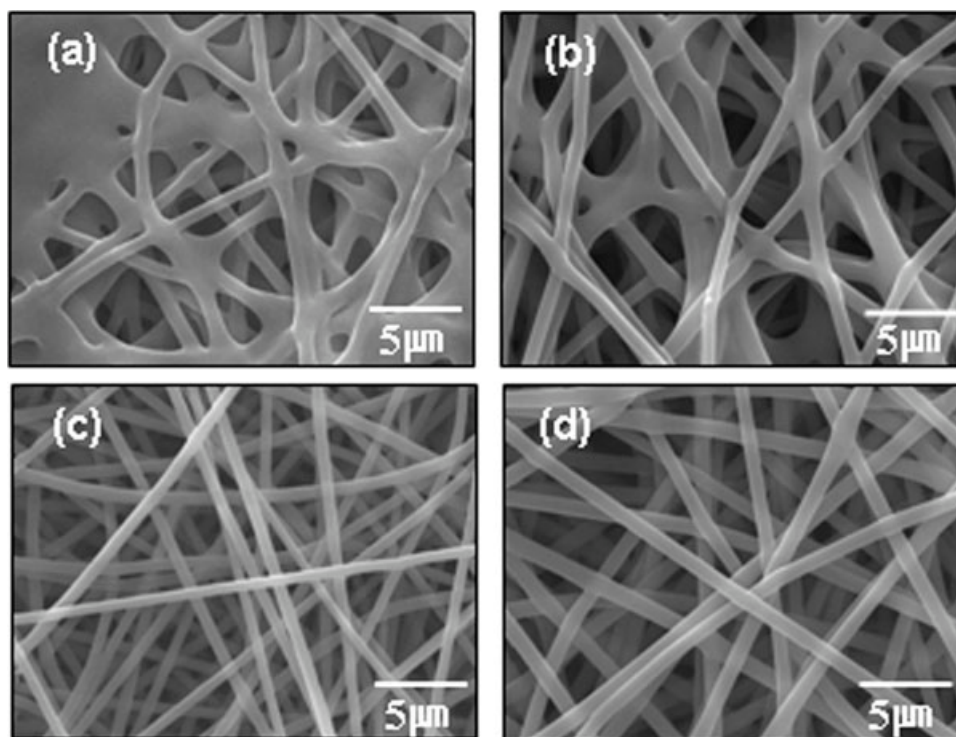


Figure 2 SEM images of PVA/COS blend submicrometer fibers synthesized with various distances between the tip and collector: (a) 5, (b) 10, (c) 15, and (d) 20 cm (PVA/COS mass ratio = 8/2, total polymer concentration = 12.5 wt %, applied voltage = 15 kV).

different electrospinning instrument parameters, including the electric voltage and tip-to-collector distance (TCD), and solution parameters, such as the polymer concentration and feed mass ratio, to determine their effects on the morphology of the fibers.

Effects of the instrument parameters

Voltage

A series of experiments were carried out: the applied voltage was varied from 5 to 20 kV, and optimum conditions (total concentration = 12.5 wt %, PVA/COS mass ratio = 8/2, tip-to-target distance = 15 cm) were used. The morphological structure could be slightly altered by changes in the applied voltage, as shown in Figure 1. At a low voltage (5 kV), numerous beads were observed [Fig. 1(a)], and when the voltage was increased to 10 kV, both beads and fibers were seen [Fig. 1(b)]. At a high voltage (20 kV), nonuniform, ribbonlike PVA/COS fibers with larger diameters were found [Fig. 1(d)]. As shown in Figure 1(c), the best result for uniform PVA/COS fibers with an average diameter of ~ 300 nm was obtained with an applied voltage of 15 kV. The results clearly demonstrated that the applied voltage played an important role in controlling the PVA/COS submicrometer fiber morphology.

Tip-to-target distance

The tip-to-target distance also had a significant effect on the electrospun PVA/COS fibers, as shown in Figure 2. Four different TCDs (e.g., 5, 10, 15, and 20 cm) were studied, and it was found that the TCD of 15 cm was ideal for synthesizing uniform submicrometer PVA/COS fibers [Fig. 2(c)].

Effects of the solution parameters: The total polymer concentration and mass ratio

Changing the total polymer concentration and the mass ratio of PVA to COS could alter the fiber diameter and morphology very effectively, as shown in Figures 3–6. With a fixed applied voltage (15 kV) and TCD (15 cm), we used total polymer concentrations of 7.5, 10, 12.5, and 15 wt % with PVA/COS mass ratios of 10/0, 8/2, and 6/4, respectively. It should be noted that when the PVA/COS mass ratio in the blend solutions increased to 5/5, the viscosity of the solution was very low, and electrospinning could not be conducted under this low-viscosity condition. Therefore, the maximum mass ratio of PVA to COS in the blend solutions was 6/4 for this study. When different total polymer concentrations and mass ratios were used, the following results were observed:

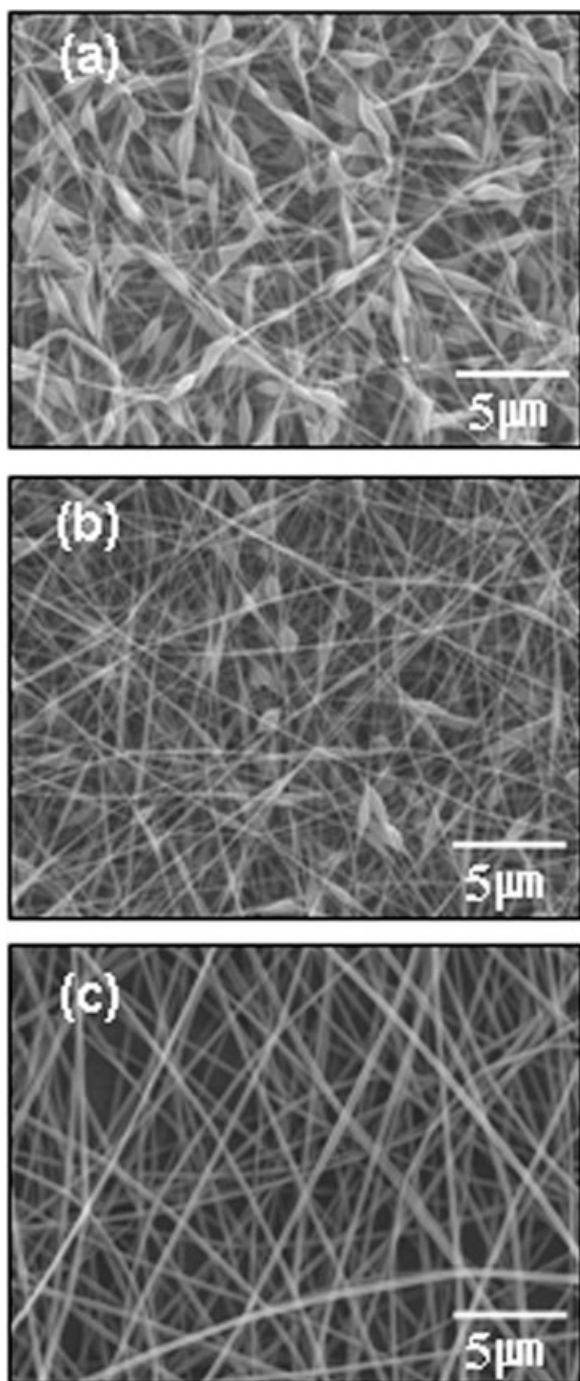


Figure 3 SEM images of PVA/COS blend submicrometer fibers electrospun with various PVA/COS mass ratios: (a) 6/4, (b) 8/2, and (c) 10/0 (applied voltage = 15 kV, total polymer concentration = 7.5 wt %, TCD = 15 cm).

1. At the 7.5 wt % total polymer concentration: With a PVA bulk solution, nonhomogeneous fibers with average diameters around ~ 220 nm were obtained [Fig. 3(c)]. However, with COS in the blend polymer concentrations, that is, with PVA/COS mass ratios of 6/4 and 8/2, fibers with a diameter of ≤ 100 nm, connected

by some beads, were found, as shown in Figure 3(a,b), respectively.

2. At the 10 wt % total polymer concentration: Similar morphological behavior was observed at a total polymer concentration of 10 wt %. With a bulk PVA solution, nonhomogeneous fibers with larger diameters around ~ 550 nm were obtained [Fig. 4(c)]. However, as shown in Figure 4(a, b), the polymer blends with a 6/4 or

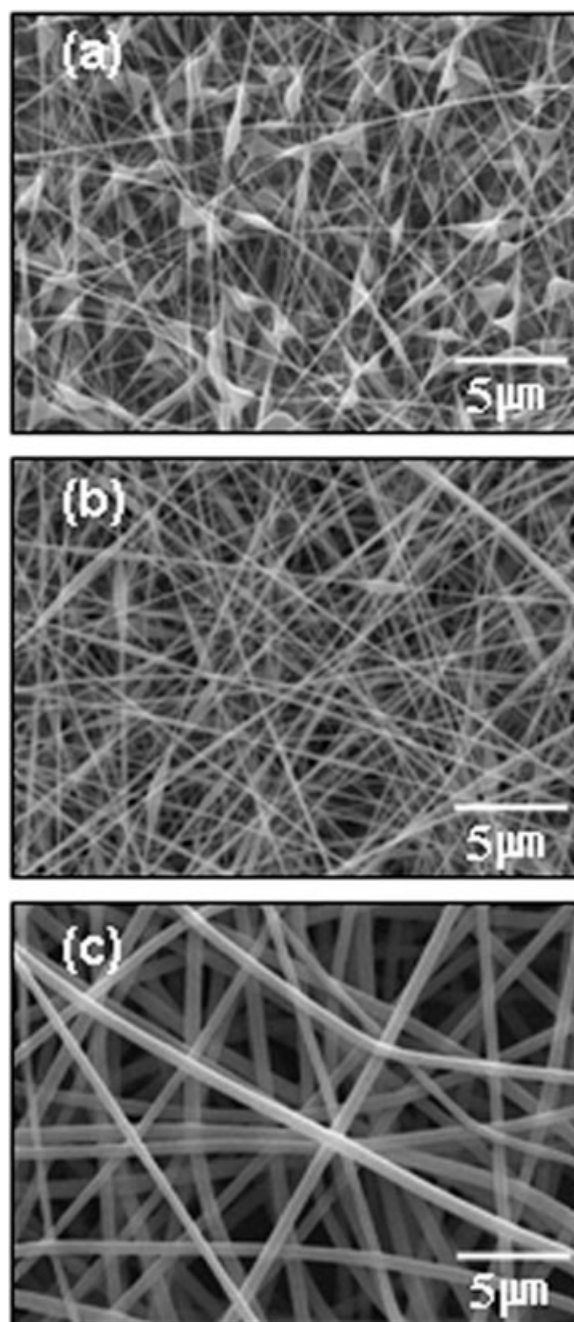


Figure 4 SEM images of PVA/COS blend submicrometer fibers electrospun with various PVA/COS mass ratios: (a) 6/4, (b) 8/2, and (c) 10/0 (applied voltage = 15 kV, total polymer concentration = 10.0 wt %, TCD = 15 cm).

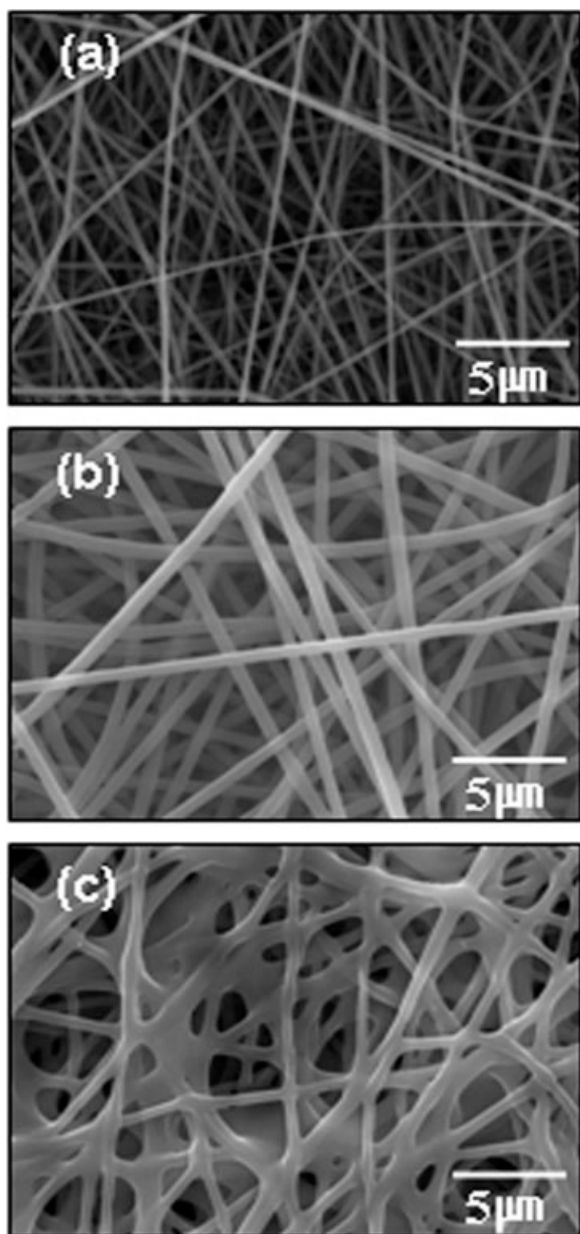


Figure 5 SEM images of PVA/COS blend submicrometer fibers electrospun with various PVA/COS mass ratios: (a) 6/4, (b) 8/2, and (c) 10/0 (applied voltage = 15 kV, total polymer concentration = 12.5 wt %, TCD = 15 cm).

8/2 PVA/COS ratio resulted in thin fibers with diameters of ≤ 150 nm with a small number of bead connections. In comparison with the results shown in Figure 3(a,b), fewer beads were found at the total polymer concentration of 10 wt %.

- At the 12.5 wt % total polymer concentration: Uniform fibers with diameters of 200–400 nm were obtained, and no beads were observed for PVA/COS ratios of 6/4 and 8/2. It was also noticed that the fiber diameter of PVA/COS was ~ 200 nm at a PVA/COS mass ratio of 6/

4, which was much smaller than the diameter of fibers obtained at a PVA/COS ratio of 8/2 when other parameters remained unchanged, as shown in Figure 5(a,b).

- At the 15 wt % total polymer concentration: A morphological trend similar to that for the total polymer concentration of 12.5 wt % was observed (Fig. 6). At the PVA/COS mass ratio of 6/4, the fiber diameter was greater than 450

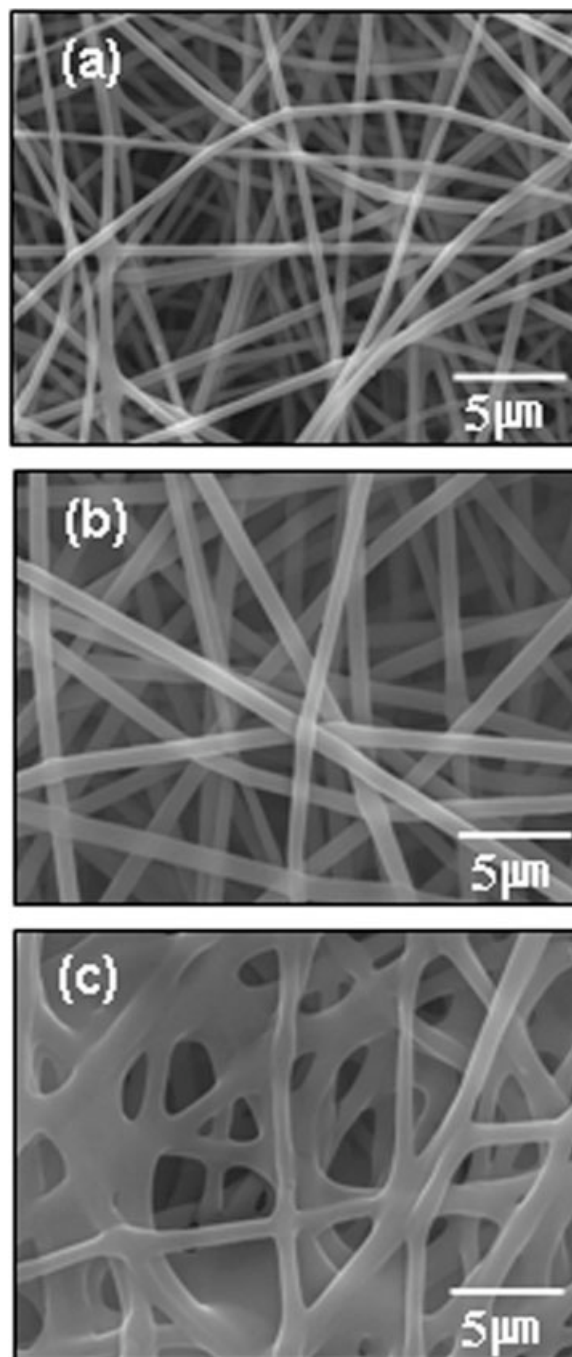


Figure 6 SEM images of PVA/COS blend submicrometer fibers electrospun with various PVA/COS mass ratios: (a) 6/4, (b) 8/2, and (c) 10/0 (applied voltage = 15 kV, total polymer concentration = 15.0 wt %, TCD = 15 cm).

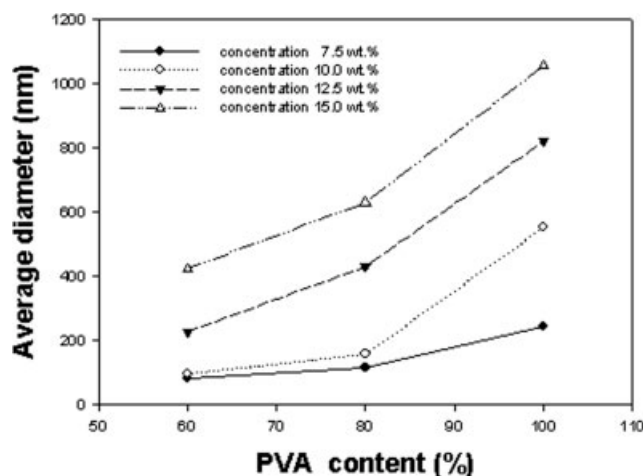


Figure 7 Average diameters of blend submicrometer fibers electrospun under various conditions (applied voltage = 15 kV, TCD = 15 cm).

nm, and uniform fibers could be electrospun easily [Fig. 6(a)]. However, at a lower mass ratio of COS in the blend (PVA/COS = 8/2) or with pure PVA, fibers with irregular diameters were found [Fig. 6(b,c)].

It can be concluded from these results that the concentration and mass ratio of the PVA/COS blend solutions were two important parameters that had remarkable effects on the morphology of the electrospun submicrometer fibers of the PVA/COS blends. To obtain uniform electrospun fibers, it was necessary to keep the PVA/COS concentration at 12.5 wt % and the mass ratio between 20 and 40 wt % COS (see Fig. 7 for the relations between the polymer concentration, mass ratio, and average fiber diameter).

Tensile strength and thermal properties

Some of the fascination with the behavior of polymers comes from the large changes in the physical properties and the wide range of mechanical behaviors.³⁰ The tensile strength of the PVA/COS blend submicrometer fibers increased with the weight percentage of COS decreasing, as shown in Figure 8. At higher weight percentages of PVA and COS (6/4), the lowest tensile strength of the PVA/COS blend fibers was observed, and this showed lower mechanical properties than the bulk PVA for all the polymer concentrations.

Figure 9 shows the DSC thermograms of electrospun pristine PVA and PVA/COS blend fibers with different mass ratios at a polymer concentration of 12.5 wt %. A relatively large and sharp endothermic peak was observed at about 222.7°C [Fig. 9(a)] and was assigned to the melting temperature of pure

PVA, which had a number-average degree of polymerization of 1700, which agrees very well with reported data.^{11,31} This peak was shifted to 217.5 and 214.7°C with the addition of 20 and 40 wt % COS [Fig. 9(b,c)], respectively, and these gradually shifted the melting temperature to lower values; this occurred because of the addition of COS. This was because the majority of the chains were in a non-crystalline state due to the rapid solidification process of stretched chains during electrospinning.

Generally, when PVA is pyrolyzed in the absence of oxygen, it undergoes dehydration and depolymerization at temperatures greater than 200 and 400°C, respectively. The actual depolymerization temperature depends on the structure, molecular weight, and conformation of the polymer. Tsuchiya and Sumi³² reported that after water molecules are eliminated from a PVA chain at 245°C, it forms a conjugated polyene structure.³² Meanwhile, three weight-loss peaks were observed in the TGA curve for bulk PVA [Fig. 10(a)]. The first peak at 25–60°C was due to moisture vaporization, the second peak at 260–380°C was due to the thermal degradation of PVA, and the third peak at 430–460°C was due to the byproduct formation of PVA during the TGA thermal degradation process. According to Holland and Hay's report,³³ thermal degradation could lead to the production of aldehyde and alkene end groups in the molten state, which could lead to the formation of a vinyl ester by the rearrangement. Figure 10(b,c) shows a similar thermogram trend for PVA/COS blend submicrometer fibers with 8/2 and 6/4 mass ratios, respectively. Clearly, it can be concluded that higher thermal properties could be obtained with a higher mass ratio of COS in the PVA/COS blend electrospinning fiber mats.

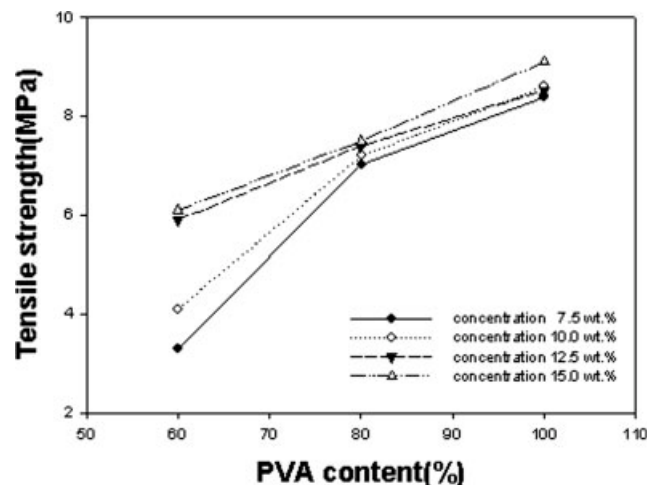


Figure 8 Tensile strengths of blend submicrometer fibers electrospun under various conditions (applied voltage = 15 kV, TCD = 15 cm).

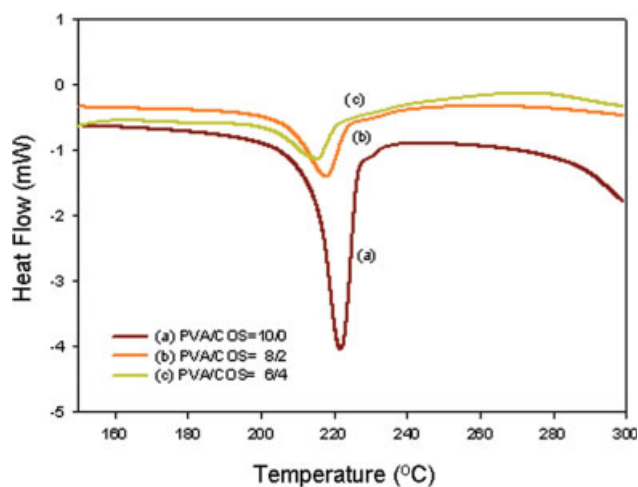


Figure 9 DSC thermograms of PVA/COS blend submicrometer fibers electrospun with various PVA/COS mass ratios (TCD = 15 cm, applied voltage = 15 kV, total polymer concentration = 12.5 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FTIR spectra

Figure 11 shows the FTIR spectra of electrospun pristine PVA and PVA/COS blend fibers of different mass ratios at a polymer concentration of 12.5 wt %. The frequencies and assignments for the pristine PVA are indicated as follows: 2944 cm^{-1} for the $-\text{CH}_2$ group stretching vibration, 1096 cm^{-1} for the C—O group, and 3413 cm^{-1} for the stretching vibration peak of its side hydroxyl groups [Fig. 11(a)]. With the addition of COS, the absorption peaks

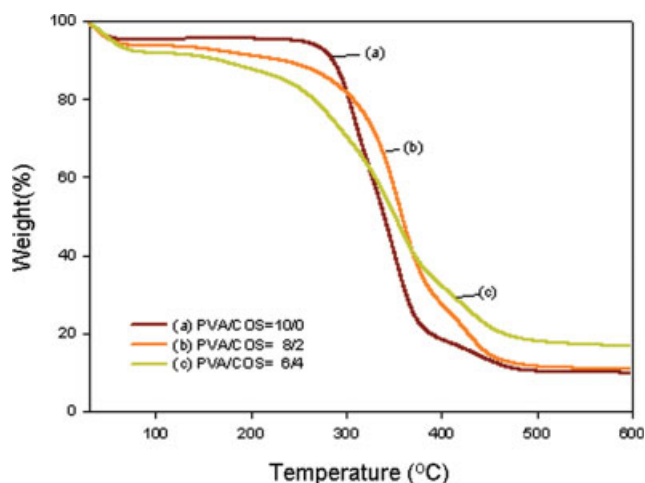


Figure 10 TGA data of electrospun PVA/COS blend submicrometer fibers with various PVA/COS mass ratios (TCD = 15 cm, applied voltage = 15 kV, total polymer concentration = 12.5 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

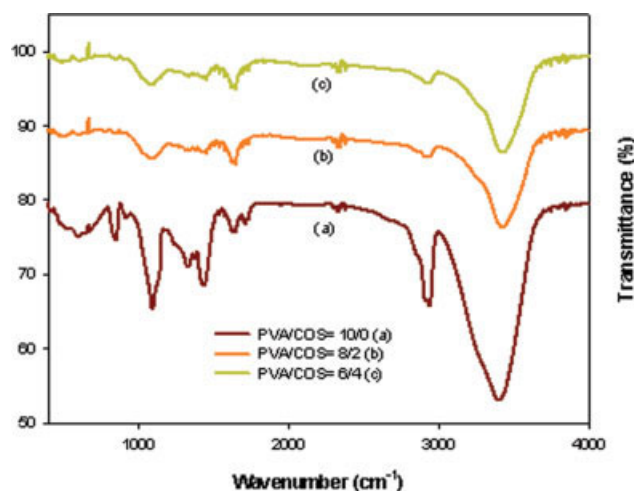


Figure 11 FTIR data of electrospun PVA/COS blend submicrometer fibers with various PVA/COS mass ratios (TCD = 15 cm, applied voltage = 15 kV, total polymer concentration = 12.5 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

became lower in intensity [Fig. 11(b,c)]. The absorption peaks at 849, 1092, 1336, 1443, and 2944 cm^{-1} gradually decreased, and some peaks disappeared because of the increasing amount of COS in the electrospun fiber mat as well as the interaction between the PVA and COS macromolecules.²⁷ This suggested that hydrogen bonds between hydroxyl groups in PVA and amino groups or hydroxyl groups in COS could possibly play a role in the shift of the peaks. Therefore, the addition of PVA could moderate the interaction between COS macromolecules and thus

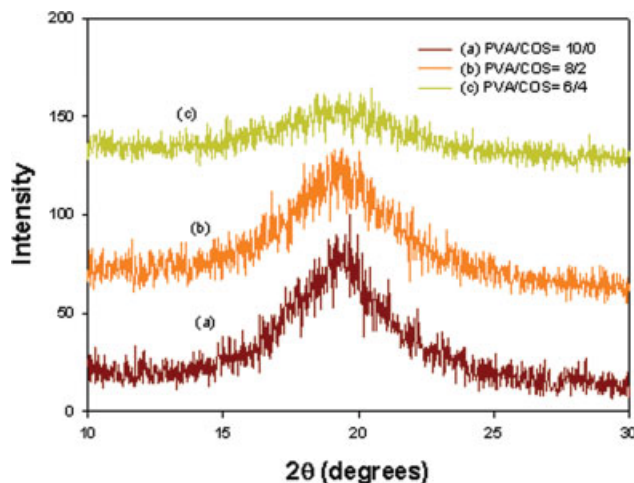


Figure 12 XRD data of electrospun PVA/COS blend submicrometer fibers with various PVA/COS mass ratios (TCD = 15 cm, applied voltage = 15 kV, total polymer concentration = 12.5 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

improve the electrospinnability of COS with PVA. The following analysis of XRD could further confirm this assumption.

XRD data

The XRD patterns of the same specimens used for the FTIR measurements are presented in Figure 12. The pristine PVA fiber mat showed a significant crystalline peak at about 19.3° , which was due to the occurrence of strong intermolecular and intramolecular hydrogen bonding [Fig. 12(a)].²⁶ As the amount of COS in the PVA/COS blend fibers was increased, the intensity of the diffraction peak at about 19.3° of pristine PVA became lower and broader [Fig. 12(b,c)]. This suggested that the crystallinity of PVA/COS fibers with higher amounts of COS (8/2 and 6/4 mass ratios) was lower than that of the electrospun PVA fiber. The reduction of the crystallinity of the electrospun PVA/COS fibers can probably be attributed to the hydrogen-bonding interaction between COS and PVA macromolecules. XRD and FTIR results indicated that PVA could possibly interact with COS through hydrogen bonding between hydroxyl groups in PVA and the amino or hydroxyl groups in COS. Therefore, the strong molecular interactions and crystalline structure of COS were hindered by the addition of PVA. Subsequently, the electrospinnability of COS with PVA was greatly improved.

CONCLUSIONS

Ultrafine PVA/COS blend fibers were produced by the electrospinning method in aqueous solutions. The polymer concentration, mass ratio of the two polymers, applied voltage, and TCDs were the main important factors influencing the electrospinnability of the PVA/COS solutions as well as the morphology of the electrospun submicrometer fibers. Uniform PVA/COS fibers with an average diameter of a submicrometer scale (200–400 nm) were prepared from a 12.5 wt % solution of PVA/COS blends with various mass ratios. At low concentrations of the total polymer blend (7.5 and 10 wt %), beads were observed in the fiber morphology for different mass ratios of PVA to COS. However, at low concentrations of the total polymer blend (15 wt %), larger diameter (>450 nm), ribbonlike fibers were produced. It might be concluded that the best synthesis conditions for the ultrafine PVA/COS blend fibers by the electrospinning technique were a polymer concentration of 12.5 wt %, mass ratios between 8/2 and 6/4, an applied voltage of 15 kV, and a TCD of 15 cm. FTIR and XRD analyses suggested that hydrogen bonding between COS and PVA molecules may have occurred, so that the electrospinnability of COS

in aqueous solutions was improved with the help of PVA. The higher the COS percentage was in the PVA/COS blend fibers, the better the thermal stability was.

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