

Electrospinning of Chitosan/Poly(vinyl alcohol)/Acrylic Acid Aqueous Solutions

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ABSTRACT: Chitosan bicomponent fibers were prepared via the electrospinning of chitosan/poly(vinyl alcohol)/acrylic acid aqueous solutions with different concentrations. With a 4% acrylic acid aqueous solution, when the chitosan/poly(vinyl alcohol) mass ratios were lower than 80/20, electrospinning nanofibers could be obtained. With a 90% acrylic acid aqueous solution, when the chitosan/poly(vinyl alcohol) mass ratios were less than 95/5, good nanofibers could be electrospun. The average diameter of the nanofibers gradually decreased, and its distribution

became narrower as the poly(vinyl alcohol) concentration increased. Chitosan/poly(vinyl alcohol)/acrylic acid aqueous solutions could be electrospun at various concentrations by the adjustment of the chitosan and poly(vinyl alcohol) concentrations. The effects of the viscosity and conductivity of the blend solution on the morphologies of the fiber mats were also investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5692–5697, 2006

Key words: chitosan; fibers; viscosity

INTRODUCTION

Chitosan [CS; i.e., (1,4)-linked 2-amino-2-deoxy- β -D-glucan] is a partially N-deacetylated derivative of chitin, which is the second most abundant natural polysaccharide in the world next to cellulose. Because CS has many useful properties, such as biocompatibility,¹ biodegradability,² renewability, antimicrobial activity,^{3,4} wound-healing properties, and antitumor effects, much attention has been paid to its potential use in wound dressings,⁵ wound healing,⁶ drug delivery systems,⁷ and various tissue-engineering applications.^{8,9} Both CS and chitin are linear polymers, and chitin is known to form a microfibrillar arrangement in shrimp shells and crabs; they are good candidates for fiber spinning.¹⁰

In past decades, electrospinning has attracted great attention because it can produce polymer nanofibers with diameters ranging from several micrometers to tens of nanometers, that is, 100–10,000 times smaller than those prepared by the traditional methods of solution and melt spinning.^{11–13} In a typical electrospinning process, a high voltage is applied to create electrically charged jets of a polymer solution. The jets dry and form nanofibers, which are collected on a target as a nonwoven mat. Because of unique properties,

such as high specific surface areas and high porosities, these nanofibers are of considerable interest for various kinds of applications, such as tissue engineering,¹² sensors,¹⁴ protective clothing,¹⁵ filter applications,¹⁶ and fiber templates for the preparation of functional nanotubes.^{17,18}

There have been several reports on the electrospinning of CS, but much remains to be explored and improved. The major complications in electrospinning CS are the poor solubility of CS, the high viscosity of its aqueous solutions,¹⁹ and the large electrical conductivities of its solutions.²⁰ The electrospinning of a pure CS solution was reported by Yamamoto et al.²¹ and Jang et al.²² The former reported that the electrospinning of a homogeneous CS nanofiber with a trifluoroacetic acid/dichloromethane solvent because of the high volatility of the solvent, and in his paper, a CS/poly(vinyl alcohol) (PVA) blend nanofiber with diluted formic acid as a solvent was also produced. The latter electrospun and homogeneous nanofibers of pure CS dissolved in a strongly concentrated, aqueous acetic acid solution, and this was attributed to the surface tension depression produced by an increasing acetic acid concentration in water, which made electrospinning the solution easy. Others blended systems of CS with poly(ethylene oxide)¹⁰ and silk fibroin²³ and CS derivatives²⁴ made into nonwoven fabrics by electrospinning have been reported.

In this work, we prepared CS/PVA blend nanofibers with acrylic acid (AA) as a solvent. AA was chosen for two reasons: (1) an aqueous AA solution

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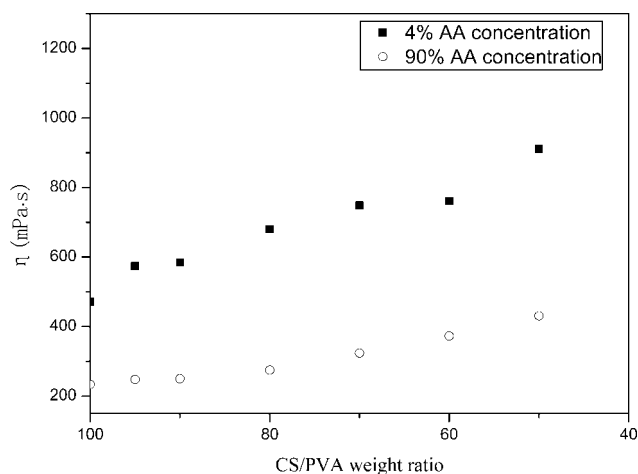


Figure 1 Viscosity (η) of the CS/PVA blend solutions.

could dissolve CS and (2) AA could easily dissolve a bifunctional acrylate monomer, which could be used to prepare crosslinkable, nonwoven fabrics with improved mechanical strength. As electrospinning from a pure CS aqueous AA solution failed, PVA was selected as the polymer additive because of its good fiber-forming and physical properties, processability, biocompatibility, and chemical resistance.^{25,26} This work investigated fiber formation from CS/PVA blend solutions with different concentrations of AA. The main focus was to determine the effects of the concentration of AA and the polymer composition on fiber formation and on the morphology of CS/PVA bicomponent fibers.

EXPERIMENTAL

Materials

CS (molecular weight = 1.2×10^5 , degree of deacetylation = 82.5%) was purchased from Zhejiang GoldenShell Biochemical Co., Ltd. (Taizhou, China). PVA (degree of polymerization = 3500; 88% hydrolyzed) was obtained from Kuraray Co., Ltd. (Tokyo, Japan). AA was from Beijing Chemical Reagents Co. (Beijing, China). All chemicals were used without further purification.

Preparation of the polymer solution

A 9% (w/v) PVA solution was prepared by the dissolution of 9.0 g of PVA in 100 mL of distilled water at 90°C with vigorous stirring for about 4 h. CS (7.0 g) was dissolved at a concentration of 7% (w/v) in 100 mL of an aqueous AA solution with AA concentrations ranging from 3 to 90% [Volume of AA/(Volume of AA + Volume of water)]. The PVA solution was mixed with CS solutions in the following CS/PVA weight ratios: 100/0, 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, and 0/100.

The shear viscosities of the solutions of different CS/PVA ratios were measured at a shear rate of 344 s^{-1} with a rotational viscometer (NDJ-79, Shanghai Jichang Geology Instrument Co., Ltd., Shanghai, China) equipped with coaxial cylinders, and the conductivities of the blend solutions also were measured with an electric conductivity meter (DDB-6200, Shanghai Rex Xinjing Instrument Co., Ltd., Shanghai, China).

Preparation of the fiber mats

The electrospinning experiments were performed at room temperature. The aforementioned mixed solutions were placed in a plastic syringe (5 mL) with a metal capillary having an inner diameter of 0.57 mm, that is, a hypodermic needle with a flat-filed tip. The positive electrode of a high-voltage power supply (BMEI Co., Ltd., Beijing, China) was connected to a metal capillary by copper wires. The voltage ranged from 15 to 30 kV, and the tip-to-collector distance was fixed at 13 cm. Grounded aluminum foil was used as the collector. The nanofibrous, nonwoven mats were collected on the surface of the aluminum foil and dried at room temperature *in vacuo* for 12 h.

Characterization

The morphology and diameter of the nanofibrous mats were determined with scanning electron microscopy (SEM; S-450, Hitachi, Ltd., Tokyo, Japan) at an accelerating voltage of 20 kV. The diameters of the nanofibers were measured with an image analyzer. Fifty fibers were used for the imaging statistics.

RESULTS AND DISCUSSION

Previous studies have shown that during the electrospinning process, physical and chemical parameters of polymer solutions, such as the viscosity, surface tension,

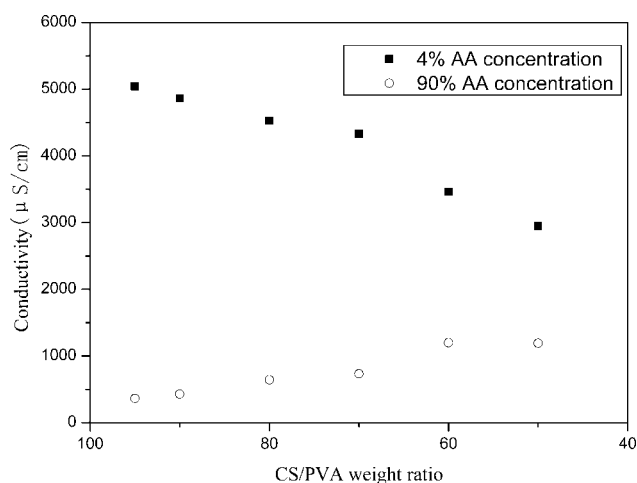


Figure 2 Conductivity of the CS/PVA blend solutions.

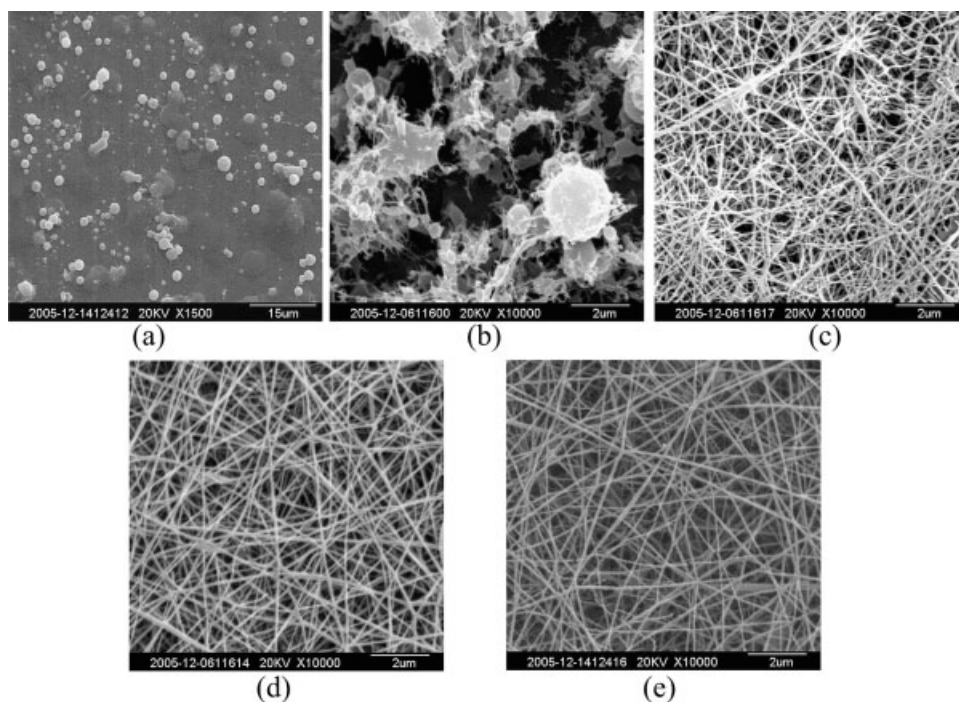


Figure 3 SEM photographs of nanofibrous mats with different CS/PVA mass ratios when the AA concentration was 4%: (a) 90 : 10, (b) 80 : 20, (c) 70 : 30, (d) 60 : 40, and (e) 50 : 50. The electrospinning voltage was 29 kV.

electric conductivity, and polymer concentration, are critical factors for the successful spinning of nanofibers.²⁷

Figure 1 presents a plot of the solution viscosity versus the weight ratio of CS to PVA in blends. The solution viscosities of the CS/PVA blends increased

with decreasing CS content whether the concentration of AA was 4 or 90%, but the viscosities of the solutions with a 90% AA concentration were obviously lower than the viscosities of the solutions with a 4% AA concentration.

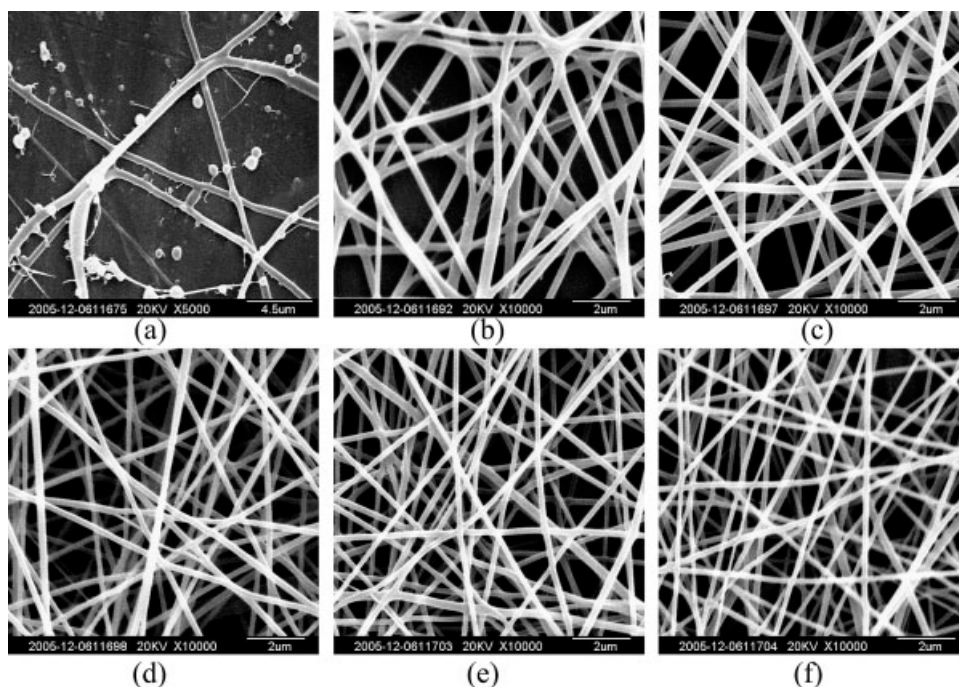


Figure 4 SEM photographs of nanofibrous mats with different CS/PVA mass ratios when the AA concentration was 90%: (a) 95 : 5, (b) 90 : 10, (c) 80 : 20, (d) 70 : 30, (e) 60 : 40, and (f) 50 : 50. The electrospinning voltage was 18 kV.

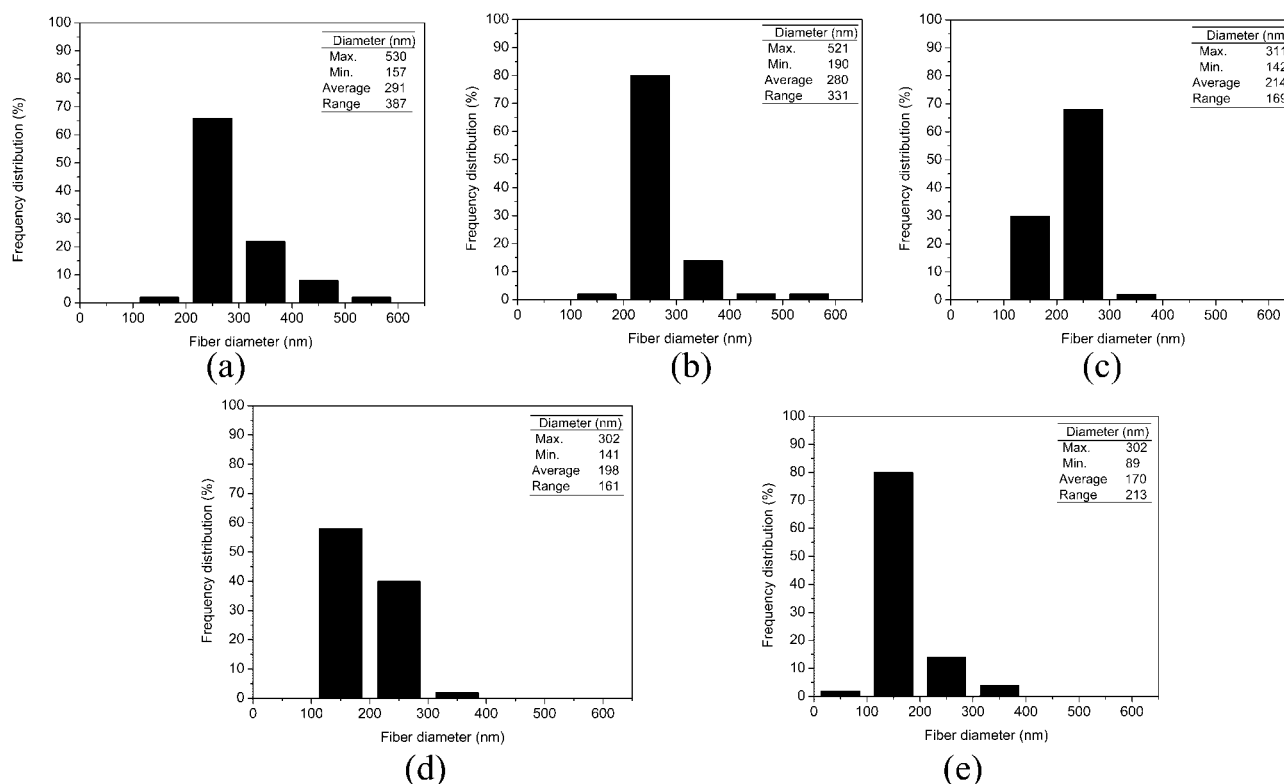


Figure 5 Nanofiber diameter distributions of nanofibrous mats with different CS/PVA mass ratios when the AA concentration was 90%: (a) 90 : 10, (b) 80 : 20, (c) 70 : 30, (d) 60 : 40, and (e) 50 : 50. The electrospinning voltage was 18 kV.

Figure 2 shows the variation in the blend solution conductivity as a function of the weight ratio of CS to PVA in the blend solutions. When the AA concentration was 4%, the conductivity of the blend solutions steadily decreased from 5040 to 2950 $\mu\text{S}/\text{cm}$ as the CS concentration changed, but when the AA concentration was 90%, the conductivity of the blend solutions gradually increased as the concentration of CS decreased from 364 (CS/PVA = 95/5) to 1192 $\mu\text{S}/\text{cm}$ (CS/PVA = 50/50); the conductivity value at CS/PVA = 95/5 was even lower than those of a pure PVA water solution (550 $\mu\text{S}/\text{cm}$). The reason might be that the degree of ionization of AA decreased with an increase in the AA concentration, and this led to a decrease in the conductivity. The conductivities of a series of blend solutions (CS/PVA = 50/50) were explored for which the AA concentration was 3, 40, 60, 80, or 90%; they were 3.98, 2.65, 2.08, 1.46, and 1.19 $\mu\text{S}/\text{cm}$, respectively. The conductivity of the blend solutions decreased with increasing AA content, and this also supports the previous conclusion.

Figure 3 shows SEM photographs of the CS/PVA blend electrospun fabrics with an AA concentration of 4%. As shown in Figure 3(a) (CS/PVA = 90/10), beads were deposited on the collector, and no obvious fibrous structure was observed. When the CS content increased (CS/PVA = 80/20), thin fibers

coexisting among the beads were observed [Fig. 3(b)]. When CS/PVA reached 70/30, beads and fibers were seen [Fig. 3(c)]. When CS/PVA was equal to or less than 60/40, the as-spun nanofibers exhibited a cross section with a smooth surface and a more regular morphology [Fig. 3(d,e)].

Figure 4 shows SEM photographs of CS/PVA blend electrospun fabrics with an AA concentration of 90%. When CS was mixed with a small portion of PVA (CS/PVA = 95/5), the coexistence of beads and fibers was observed, as shown in Figure 4(a). For electrospun nanofibers (CS/PVA = 90/10), there were some junctions and bundles of fibers [Fig. 4(b)]. Figure 4(c-f) provides the morphology of blend nanofibers of CS and PVA with different CS contents. The blend solutions became easy to electrospin with an increase in the PVA content.

Correspondingly, the average diameters and diameter distributions of nanofibrous mats are presented in Figure 5. As the CS content in the blends decreased from 90/10 to 50/50, the average diameter of the blend nanofibers gradually decreased from 291 to 170 nm and its distribution became slightly narrower. It might be thought that when a single jet splits into multiple filaments because of radical charge repulsion,²⁸ it undergoes more splaying because of increased conductivity with increasing PVA content.

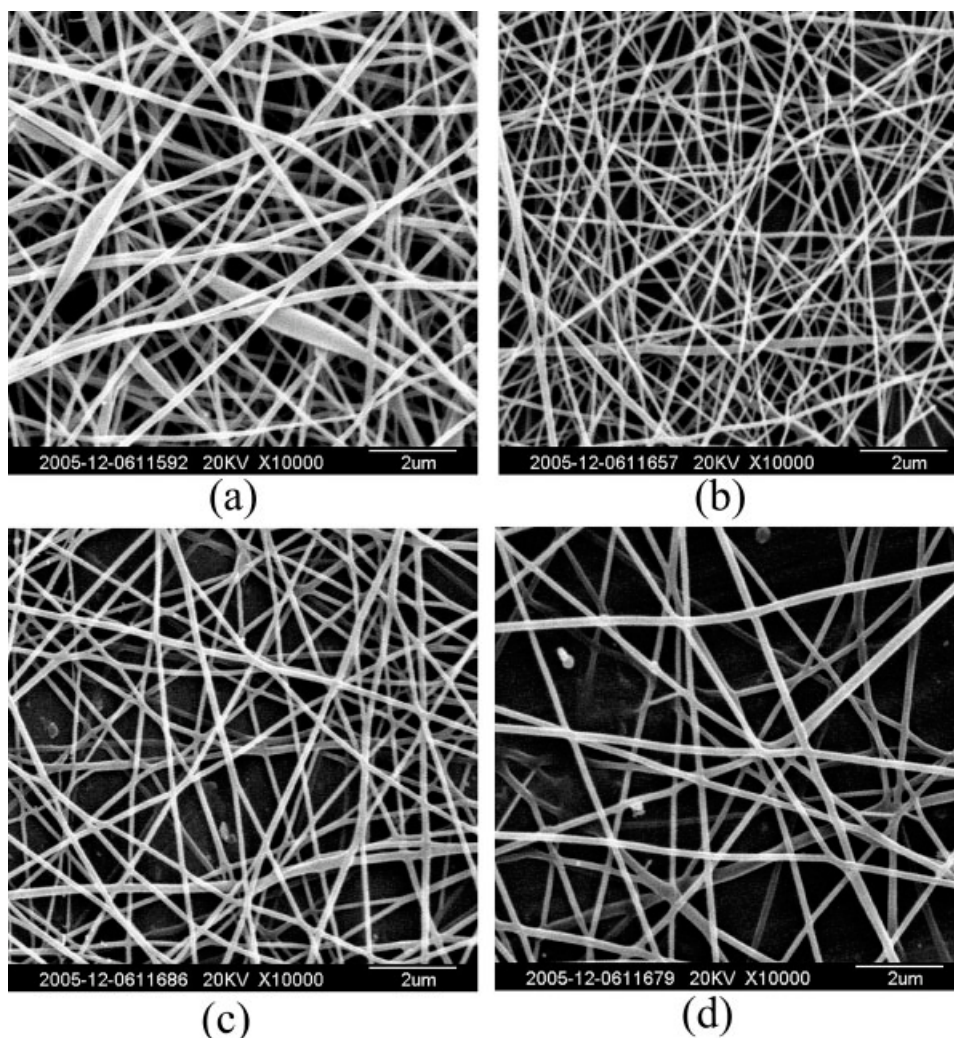


Figure 6 SEM photographs of nanofibrous mats with different AA concentrations: (a) 3, (b) 20, (c) 60, and (d) 80% (CS/PVA = 50 : 50).

Looking at Figure 3, we found that when the AA concentration was as low as 4%, the blend solutions with CS/PVA equal to or more than 80/20 could not be electrospun. However, when the AA concentration was as high as 90%, the blend solutions (CS/PVA = 90/10 or 80/20) could be electrospun very well. This might be explained by the conductivity and viscosity changes of the blend solutions. Conventional CS solution formulations displayed electrical conductivities that were unacceptably large for electrospinning.²⁰ Such liquids underwent deep atomization, that is, high charge density, and they broke into polydisperse electrosprays.²⁰ In this experiment, when the AA concentration was low (4%), the conductivities of the blend solutions were quite high even up to 5040 $\mu\text{S}/\text{cm}$; this was attributed to an increase in the degree of ionization of AA in diluted solutions. High electrical conductivity led to deep atomization of the solution, so the liquid was broken into polydisperse electrosprays, as illustrated in Fig-

ure 3(a). There were intermolecular interactions between CS and PVA, and these interactions could be caused by hydrogen bonds between the hydroxyl oxygen atoms in PVA and $-\text{NH}_2$ or $-\text{OH}$ groups in CS,^{29,30} so the degree of protonation of $-\text{NH}_2$ groups decreased in diluted AA solutions. Meanwhile, at diluted AA concentrations, the viscosities of the blend solutions were too low to be electrospinnable. With an increase in the PVA content, the conductivities of the solutions gradually fell, whereas the viscosities of the solutions increased enough to enhance the molecular entanglement necessary for fiber formation, which made the blend solutions electrospun.

When the AA concentration was high (90%), because of the lower degree of ionization of AA in the solutions, the conductivities of the blend solutions were low enough to make them electrospinnable. However, neat AA did not dissolve enough CS to be electrospinnable.

Figure 6 shows SEM photographs of nanofibrous mats with different AA concentrations. When CS/PVA was fixed at 50/50, CS/PVA blend solutions prepared with AA concentrations ranging from 3 to 90% were electrospinnable. In our experiments, we found that blend solutions with any concentration of AA (necessary to dissolve CS fully) could be electrospun as long as we could adjust CS and PVA to the proper proportions.

CONCLUSIONS

The electrospinning of CS/PVA blend solutions was performed with AA as a spinning solvent. When the AA concentration was as high as 90%, CS/PVA blend solutions with CS concentrations lower than 95% could be electrospun into a continuous fibrous structure, although pure CS aqueous AA solutions were not electrospinnable. The as-spun CS/PVA blend nanofibers had smaller diameters and narrower diameter distributions with increasing PVA content. However, as the AA concentration fell to 4%, the CS/PVA blend solutions could be electrospun into fibrous structures just when the CS concentration was lower than 70%. CS/PVA blend nanofibers could be prepared at different AA concentrations ranging from 3 to 90% by the adjustment of the CS/PVA weight ratio.

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